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Catalytic oxidation of propane

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CATALYTIC OXIDATION OF PROPANE

by

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I. SUMMARY

The production of alcohols, aldehydes, ketones and acids by the oxidation of propane is possible and economically attractive, with raw materials representing only two to twenty percent of the product selling price. Commercial non-catalytic processes now produce mixtures of these products which are difficult to separate and purify.

The high temperature catalytic oxidation of propane by oxygen was studied in a simulated fluidized bed at atmospheric pressures with no recirculation of catalyst. This process was developed in an attempt to provide the temperature control and the promotion of a specific reaction which are necessary to yield given oxygenated chemicals from oxygen and propane.

The experimental equipment provided for mixing heated, measured amounts of oxygen and propane in the presence of catalyst at various temperatures and flow rates. A mechanically-agitated bed of catalyst was used to simulate a conventional fluidized bed in a 1¼ inch pipe.

Twenty-four runs are reported, made at temperatures up to 1,000° F. on feed mixtures, containing from 10 to 30 percent oxygen, flowing at rates of 3,000 to 7,000 cc. per minute. The four catalysts of Celite and copper oxide on

Celite were not selective, producing mixtures consisting mainly of aldehydes and ketones with smaller amounts of alcohols and, occasionally, acids. These useful products contained a maximum of 3.66% of the oxygen fed. If unreacted propane were recycled, a maximum of 7.4% of the fresh carbon feed would have been converted to useful products.

With the catalysts used, temperature was most influential on the reaction, with no products found below 800° F. The temperature control demonstrated by the apparatus was found to be limited by operating temperature, feed composition and the catalyst used. In the ranges studied, feed composition and flow rate had little effect on conversion of oxygen fed. Dehydrogenation of the propane, with the formation of substantial quantities of unsaturated hydrocarbons, was found to accompany yields of useful products. The unsaturated hydrocarbons contained a maximum of 21.5% of the carbon fed. If unreacted propane were recycled, a maximum of 85.0% of the fresh carbon feed would be found as unsaturated hydrocarbons.

The investigation did not reveal the selective catalyst sought but did demonstrate the advantages of a fluidized bed for the control of exothermic reactions. The necessary analysis procedures were complicated and time consuming and limited the information obtainable.

II. INTRODUCTION

The petroleum industry has become, in a relatively short time, one of the major industries of the United States. The value of products shipped has assumed large proportions, as shown in Table 1 (44).

Table 1

Petroleum Refining. Number of Employees and Value of Products Shipped, 1947 - 1951

Year	Number of employees	Value of products shipped
1947	145,806	$6,623,708,000
1949	144,155	7,681,578,000
1950	139,125	9,410,427,000
1951	151,434	11,538,979,000

The primary products of the petroleum industry are used for fuel. In 1947, gasoline represented 47.3% of the value of the output of the industry, fuel oil and kerosene, 32.6% and lubricating products, 10.9%. Chemicals produced by the industry, although worth $38,819,000, represented a mere 0.6% of the value of the products (44). In 1950 the President's Materials Policy Commission reported that the non-fuel utilization of hydrocarbons represented 0.7% of total hydrocarbon consumption. The Commission predicted

that in 1975, when this consumption will have expanded six times, it will represent about 2.7% of the total hydrocarbon requirements. The commission went on to report (49, p. 16):

> Nonetheless, the United States will obtain from this source most synthetic rubber, plastics, synthetic fibers, solvents and other chemicals. It is estimated that such products increase the value of the hydrocarbon raw material approximately 12 times; conversion to fuel increases the value of the raw material only 1½ times.

The most spectacular developments in the industry during the last fifteen years have been those used to improve the yield and quality of gasoline. The Houdry, Thermofor, Fluid, and Hydroforming catalytic cracking and the alkylation, polymerization and isomerization processes were all developed for these purposes.

Another important part of the petroleum industry is the production of liquefied gaseous products. These materials are gases at ordinary temperatures and pressures but can easily be liquefied by the application of moderate pressures. The most important of these gases are butane and propane. The production and sales of these gases have enjoyed steady increases during the past several years, as indicated by Table 2 (45, 46, 47, 48).

The distribution of sales among propane, butane and mixtures of the two is shown in Table 3 (48). These figures show that the sales of propane have been expanding much more rapidly than those of butane.

Table 2

Sales of Liquefied Petroleum Gases in the United States, 1933 - 1949, in Thousands of Gallons

Year	Sales
1933	38,931
1934	56,427
1935	76,855
1936	106,652
1937	141,400
1938	165,201
1939	223,580
1940	313,456
1941	462,852
1942	585,440
1943	675,223
1944	1,060,156
1945	1,276,766
1946	1,704,262
1947	2,209,797
1948	2,736,801
1949	2,836,599

Table 3

Sales of Propane and Butane in the United States, 1944 - 1949, in Thousands of Gallons

Year	Propane	Butane	Propane-butane mixtures
1944	335,884	273,116	451,156
1945	444,581	325,140	507,045
1946	551,250	441,418	711,594
1947	863,686	398,635	947,476
1948	1,279,744	512,615	944,442
1949	1,403,359	488,801	944,439

The supply of these gases is quite plentiful, for they can be obtained from natural gas, from petroleum, and from refinery gases. The average yield of liquefied petroleum gases from natural gas was only 0.50 gallon per 1,000 cubic feet treated (47), but when the total production of natural gas is considered, 7,178,777,000,000 cubic feet in 1948 (47), this source assumes its relative importance. During 1949, refineries in the United States produced 23,144,000 barrels of liquefied gases (48). That the future supply is assured is shown by a report of the American Petroleum Institute and the American Gas Association on December 31, 1949, indicating that the proved reserves of natural-gas liquids, including condensate, natural gasoline and liquefied petroleum gas liquids, was 3,729,012,000 barrels (48).

Propane is much more useful than butane as a source of chemicals other than synthetic rubber. This is shown in Table 4 (48) which gives the sales distribution or uses of these gases in 1949. This table also shows that the chief single use of propane either alone or in mixtures, is as a source of domestic and commercial heat and power. Propane, because of its longer chain length, is more reactive than either methane or ethane, the lower members of the saturated hydrocarbon series. It can be subjected to pyrolysis, to chlorination, to nitration and to oxidation to give a wide variety of products.

Table 4

Sales of Liquefied Petroleum Gases in the United States, by Use, 1949, in Thousands of Gallons

Use	Propane	Butane	Propane-butane mixture	Total
Domestic and commercial	854,456	154,599	618,495	1,627,550
Gas manufacturing	144,883	61,501	32,826	239,210
Industrial plants	99,736	43,343	19,118	162,197
Synthetic rubber	1,380	156,607	19,863	177,850
Chemical plants	277,045	56,476	211,365	544,886
Internal combustion	20,264	14,993	42,724	77,981
All other	5,595	1,282	48	6,925
Total	1,403,359	488,801	944,439	2,836,599

Oxidation of propane is a very promising field because of the large number of useful products. Not only are the three-carbon oxygenated derivatives of propane found, but it is also possible to obtain the oxygenated derivatives of methane and ethane. Normal and iso-propyl alcohol, propionaldehyde, propionic acid, acetone, ethanol, acetaldehyde, acetic acid, methanol, formaldehyde and formic acid, among others, have been reported (21) as oxidation products of propane.

The oxidizing agent generally employed is oxygen, either pure or in mixtures such as air. Kiddoo has pointed out (25) the selection of the form of oxygen to be used is generally a matter of an economic balance. The addition of nitrogen or steam has been used to control the nature of the reaction. Presently, oxygen can be obtained in purities above 99.9% at a cost of $1.30 per 100 cubic feet (17). However, one of the most promising developments in the field of oxidation is the introduction of tonnage oxygen of 90 - 95% purity. Marek has reported estimates of costs for tonnage oxygen ranging from one dollar per ton (29) to $9.70 per ton (30) depending on the size of the plant installed. An actual cost of $5.00 per ton for an operating plant has been reported (30). Various oxygenated chemicals can be produced from propane and oxygen by the reactions shown in Table 5.

The current cost of propane is $0.04 per gallon or $0.0095 per pound (17). Based on these costs and the reactions given in Table 5, the cost of reactants to produce oxygenated products worth $1.00 is reported in Table 6 using various sources of oxygen. The prices of the various chemicals are from the current literature (17). This

Table 5

Reactions to Produce Various Oxygenated Products from Propane and Oxygen

Product	Reaction
Methanol	$C_3H_8 + 2\ O_2 \rightarrow 2\ CH_3OH + CO_2$
Formaldehyde	$C_3H_8 + 2\ O_2 \rightarrow 3\ HCHO + H_2O$
Formic acid	$C_3H_8 + 3.5\ O_2 \rightarrow 3\ HCOOH + H_2O$
Ethanol	$2\ C_3H_8 + 4\ O_2 \rightarrow 2\ C_2H_5OH + 2\ H_2O + 2\ CO_2$
Acetaldehyde	$2\ C_3H_8 + 2.5\ O_2 \rightarrow 3\ CH_3CHO + 2\ H_2O$
Acetic acid	$2\ C_3H_8 + 4\ O_2 \rightarrow 3\ CH_3COOH + 2\ H_2O$
Acetone	$C_3H_8 + 2\ O_2 \rightarrow CH_3COCH_3 + 2\ H_2O$
Acrolein	$C_3H_8 + 1.5\ O_2 \rightarrow CH_2{=}CHCHO + 2\ H_2O$

table shows that it would be impossible to produce the products using pure oxygen as a raw material because of its high cost. If air were used in the process instead of high concentration oxygen, the cost of raw materials would be merely that of propane.

Table 6

Cost of Raw Materials to Produce Various Oxygenated Products from Propane and Oxygen

Product	Price[a] $ per lb.	Cost of reactants to produce products worth one dollar				
		Propane[b]	Oxygen		Total	
			At $1.30 per 100 cu. ft.	At $5.00 per ton[c]	Using O_2 at $1.30 per 100 cu. ft.	Using O_2 at $5.00 per ton[c]
Methanol	0.0485	$0.134	$2.69	$0.058	$2.82	$0.192
Formaldehyde[d]	0.042	0.041	0.814	0.017	0.855	0.058
Formic acid[e]	0.142	0.018	0.708	0.014	0.726	0.032
Ethanol[f]	0.073	0.118	2.64	0.050	2.76	0.168
Acetaldehyde	0.10	0.063	0.885	0.017	0.948	0.080
Acetic acid	0.09	0.051	1.77	0.043	1.82	0.094
Acetone	0.085	0.085	1.97	0.036	2.06	0.121
Acrolein	0.47	0.016	0.250	0.003	0.266	0.019

[a]All price data from reference 17.

[b]Cost of propane is $0.04 per gallon (17), or $0.0095 per pound.

[c]90% by weight (88.8%) by volume.

[d]37% by weight.

[e]85% by weight.

[f]190 proof.

Consideration of the raw material costs using either air or tonnage oxygen shows that either process could be economically attractive. The difference in cost of raw materials to produce products worth one dollar varies from less than one cent to about six cents. To supply the same amount of oxygen from air would require recycling and separation procedures and more pumping capacity, thus increasing building and operating costs above that of a tonnage oxygen process.

These costs are only raw material costs and involve no plant or operating costs. They are based on complete reaction of stoichiometric amounts of reactants according to the reactions listed in Table 5. However, there is a considerable margin which should permit the absorption of plant and operating costs and still leave enough return to make production profitable.

The possible products would include some of the chemicals now in greatest demand in the country. Table 7 shows the yearly production during recent years of selected members of the group (50). It can be seen that the demand is great and is steadily increasing.

With the large market available and the apparent economic attractiveness of production of these oxygenated products of propane the question arises as to why this method is not now employed for the commercial production of

Table 7

Production of Selected Organic Chemicals in the United States, 1944 - 1951, in Thousands of Pounds

Year	Synthetic methanol	Formaldehyde	Formic acid	Synthetic ethanol	Acetaldehyde	Acetic acid	Acetone
1944	472,686	522,440				292,611	328,428
1945	493,110	423,689				267,518	307,363
1946	509,820	458,877			351,916	285,452	298,148
1947	555,481	520,642			424,645	362,463	357,193
1948	990,240	617,187			471,148	396,038	443,750
1949	838,803	549,744	14,947	653,189		349,526	388,139
1950	901,584	835,142	15,703	735,440		441,166	458,786
1951	1,223,798	987,456	16,960	856,913		454,010	538,448

these compounds. Actually, similar methods are employed, but to a limited extent. To date it has been impossible to produce specific compounds from propane and oxygen. A mixture of products, very difficult to separate into the various compounds at competitive prices, is obtained. Currently, three companies -- Celanese Corporation of America, Cities Service Oil Company and Commercial Solvents Corporation -- are engaged in the production of formaldehyde and other oxygenated products by the direct oxidation of petroleum gases (55). Their combined capacity amounted to about 16% of the total formaldehyde capacity in 1950 or about 210 million pounds per year. The Celanese process accounts for 180 million pounds and involves the oxidation of a propane-butane mixture with air non-catalytically at temperatures of 600 to 1,000° F. and pressures of 100 to 300 psi. The ultimate yield of salable chemicals is estimated to be 50% of the fresh carbon feed (25). The Cities Service process, with a capacity of 25 million pounds per year, is very similar but employs natural gas and air rather than the propane-butane mixture and air.

There is a very definite need for a process to produce specific oxygenated chemicals from oxygen and hydrocarbons in similar commercial amounts. The cost of present processes is concentrated in the separation and purification equipment made necessary by the complex mixtures obtained. If these

processes resulted in single compounds this cost could be avoided and the production expanded. One of the methods to accomplish this would be the utilization of a suitable catalyst to direct the reaction to a single given compound, resulting in reduced separation costs. If, in addition, this catalyst could be made to promote the reaction at lower temperatures and pressures, equipment would be simplified and its cost reduced.

The ideal process would be one which could be adapted to produce different compounds by simply changing catalysts, or by changing operating conditions with a given catalyst. This is a report of the design and operation of apparatus used to test several catalysts.

III. LITERATURE REVIEW

Only during the last decade has direct oxidation of hydrocarbons to oxygenated chemicals assumed major importance although this process has been practiced commercially in this country for more than 25 years. Research along these lines has been going on for more than 40 years (25).

In 1906 Bone and Drugman found liquid products in the oxidation of propane and butane (12). Lind and Bardwell reported liquid products other than water in 1926 (28). James, at the same time, produced aldehydes and acids from natural gas and oxygen using molybdic acid as a catalyst at temperatures less than 600° C. and pressures of 3.5 atmospheres (24). Bludworth has been particularly active in this field. One of his early patents was granted in 1933 for a high pressure, non-catalytic oxidation of propane and butane (8). He has made many contributions to a non-catalytic, high pressure process involving steam and air, a very brief reaction time, and a water quench. Pressures mentioned are 3.5 to 30 atmospheres with temperatures of 550 to 750° F. (7, 8, 9, 10, 11).

The non-catalytic production of formaldehyde, acetic acid, methanol and propanol has been noted in the literature. Propane and butane were oxidized with 5 to 15% oxygen under

pressures of 130 to 170 atmospheres and temperatures of 280 to 350° C. with up to 40% of the oxygen fed appearing in the products (54). The Hanlon-Buchanan Company developed a process for the partial oxidation of refinery butane using an iron reaction coil and employing high temperatures and pressures to produce oxygenated products (35).

One somewhat unique series of investigations has been that of Rust, Bell and others for the Shell Development Company. They have employed a homogeneous catalytic reaction using hydrogen bromide as the catalyst, in the oxidation of ethane, methane, propane and higher hydrocarbons. Propane gives a yield of 74.7 mole percent acetone, 7.8 mole percent propionic acid and 9.6 mole percent propyl bromide. The alkyl bromides can be recycled (41, 42, 43). Straight chain paraffins above ethane, in general, go to ketones. The character of the products is determined by the most reactive C-H linkage in the molecule, the tertiary being most reactive. Small amounts of splitting of the C-C bond are noted, with low reaction temperatures, and high yields and conversions (1, 3, 4, 37). A Dutch company has been doing similar work (2).

Fujimoto has claimed the formation of dihydroxy butyl peroxide under the influence of a silent discharge (23). Hydrogen peroxide has been reported as a product of the reaction of a mixture of 90% propane and 10% oxygen by

Lacamble (27) and Kooijman (26). Newitt and Schmidt studied the reaction of propane and air in ratios from 1:20 to 1:0.5 at pressure up to 100 atmospheres and temperatures of 250 to 373° C. to yield isopropyl, n-propyl and methyl alcohols and acetone (38).

DeWitt and Hein at Michigan State College have investigated the oxidation of methane, ethane and propane with oxygen and nitrogen using fairly low concentrations of oxygen (20%). Their work was done at atmospheric pressure with temperatures up to 650° C. Various catalysts including copper turnings, silica gel, and copper, vanadium and molybdenum oxides on silica gel were used to form formaldehyde and formic acid in yields to about three percent of the oxygen fed (20). Dodge and his co-workers have reported extensive investigation of the oxidation of four-carbon hydrocarbons by air, using vanadium pentoxide in the 10 to 14 mesh screen size as a catalyst, to yield maleic and acetic acids, formaldehyde, acetaldehyde and glyoxal. Butane did not react under conditions causing reaction of unsaturated hydrocarbons (13). Natural gas has been combined with oxygen to form synthesis gas, which is then converted to synthetic fuels (36).

Another interesting process is one which avoids the needs of producing oxygen gas or using air with the dilution introduced by the inert nitrogen. The use of intermediate

metal oxides as oxygen carriers has been suggested for the conversion of methane to carbon monoxide - hydrogen mixtures (52, 53). A fluidized bed technique using finely divided iron or copper oxides along with nickel on alumina as well as iron and manganese oxides has been effective (18, 52, 53). The fluidized bed technique has also been used in the oxidation of ethylene to the oxide (32).

Propylene has been oxidized directly to acrolein by the Shell Chemical Company by a process in which propylene plus air or oxygen plus a moderate catalyst poison is passed over a copper oxide catalyst (15, 16, 39).

Several reviews on recent developments on the oxidation process by Marek have appeared in the five annual Unit Processes reviews appearing in Industrial and Engineering Chemistry (29, 30, 31, 32, 33).

Not too much has been published about the details of the commercial processes. The Celanese plant at Bishop, Texas is a post war $20,000,000 installation based on the controlled, non-catalytic oxidation of propane and butane hydrocarbons and is reported to consume over 50,000,000 gallons of these materials annually (5, 6). Over 300,000,000 pounds of chemicals are shipped each year. A Canadian plant based on the same process and another Texas plant have also been built by this company.

The Cities Service Company's natural gas oxidation

plant at Tallant, Oklahoma yields a crude liquor reported to contain 35% methanol, 20% formaldehyde, 5% acetaldehyde and varying amounts of higher alcohols and aldehydes plus acids from natural gas and air (51). A review of these two successful commercial operations has been given by Kiddoo (25).

One of the ill-fated commercial adventures in this field has been that of the McCarthy Chemical Company at Winnie, Texas. The plant was reported to employ a direct oxidation technique to manufacture 600,000 to 900,000 pounds per day of acetaldehyde and formaldehyde (7). Its use of tonnage oxygen to oxidize 100,000,000 cubic feet of natural gas daily was announced in 1949 (31). After a short period of operation, the plant was shut down early in 1950 and has not been reopened. Two difficulties, inadequate conversion of the oxygen to products of value and difficulties in the recovery and purification of valuable products, apparently made the operation uneconomical.

IV. EXPERIMENTAL

The utility of a catalyst in the promotion and direction of the oxidation of hydrocarbons was noted in the introduction. The function of a catalyst normally depends on the amount of surface which the catalyst can present to the reactant materials and on the ability of the reactants to come in contact with these surfaces.

The oxidation of hydrocarbons is a highly exothermic reaction as evidenced by their wide use as fuels. The formation of formaldehyde from propane and oxygen by the reaction

$$C_3H_8 + 2\ O_2 \longrightarrow 3\ HCHO + H_2O$$

has an exothermic heat of reaction of 128,620 calories per gram mole of propane. When this reaction or others similar to it are carried out in a fixed catalyst bed, this large amount of heat is liberated in a very small space and causes localized high temperature conditions or hot spots. These excessive temperatures cause the reaction to proceed to carbon dioxide and water and, in addition, promote the cracking of the hydrocarbon with accompanying formation of carbon on the catalyst. This deposit of carbon may eventually foul the catalyst or block the passages for flow.

A fluidized bed of catalyst offered the most promising solution of these problems. Fluidization is a unit operation which maintains a bed of finely divided solids in a turbulent dense state by a gas flow moving up through the mass, giving it a resemblance to a boiling liquid. The application of fluidization to catalysis received a tremendous impetus during the second World War when it was applied to the catalytic cracking of oil to produce high octane gasoline. Since then, numerous installations of this type, some capable of processing up to 60,000 barrels a day, have been made and "fluid cat crackers" are the back bone of catalytic cracking in the oil industry.

The temperatures in a fluidized bed can be controlled quite closely. The rapid motion of the solids provides rapid mixing and gives virtually isothermal conditions in catalyst beds of 40 feet in diameter and 20 feet in height. Liberated heat is absorbed by the mass of catalyst and can be removed from the reaction zone by removal of the catalyst. This operation is possible because the solid materials can be rapidly transported in a gas stream. In the oil industry this feature is used to remove catalyst fouled by carbon deposit in the reactor and carry it to a regenerator where the carbon is burned off in a stream of air in another fluidized bed. The regenerated catalyst is then recycled to the reactor.

Heat transfer to surfaces in the bed is much higher than that usually found between gases and solids and is usually of the same order of magnitude as that found in boiling liquids. Because the individual catalyst particles are small (from below 200 mesh to above 80 mesh in some cases), the solids present a very large surface per unit weight. The surface itself is kept relatively free of gas films by the sweeping action of the gases and interparticle collisions, insuring good gas-catalyst contact.

These advantages seem well suited to the requirements of the hydrocarbon oxidation process. Fluidized beds present maximum surface area to the reactants and are capable of high heat dissipation and good temperature control. It was decided to apply a fluidized bed technique to the catalytic oxidation of hydrocarbons.

Propane was chosen as the hydrocarbon to be used in an oxidation study using pure oxygen. Propane was chosen instead of butane or mixtures of the two mainly because the possible oxidation products from propane are much less numerous than those from butane. This would simplify separation and analysis of the products and facilitate interpretation of the results. Butane, because of its greater chain length, is easier to oxidize than propane and many investigators have found that procedures developed for propane oxidation also apply to butane oxidation with little

or no modification. Thus any developments made with propane would probably also apply to butane. Propane, boiling at -42.2° F. would provide gas when stored outside during the winter whereas butane, with a boiling point of 30.9° F. would not. Butane would also be more likely to crack in the apparatus with accompanying carbon deposit because of its longer chain length.

Oxygen was used, rather than air, because it is made up completely of reactant material. Use of air would provide four parts of nitrogen for every part of air which would require larger equipment and depress the gas analysis accuracy for the same flow rates of reactants. Numerous investigations have been made using air and it was hoped to develop a process which could employ tonnage oxygen.

It was hoped to accomplish the oxidation at low pressures and no provision for high pressure operation was made. Fluidized beds are difficult to control under high pressures and these pressures add to the complexity of the equipment. High temperatures are necessary for this type of study so provisions for heating the reactant gases were made.

The only reasons for catalyst circulation in this type of equipment are for heat removal or regeneration of fouled catalyst. Recirculation and its complex equipment were avoided because the equipment was designed to remove heat through the walls, and it was unnecessary to regenerate

the catalyst until it had been demonstrated that it actually was fouled.

The process tested thus involved the catalytic oxidation of propane with oxygen at high temperatures in a fluidized bed at atmospheric pressure with no recirculation of the catalyst.

A. Glass Prototype

An apparatus was then built to provide the fluidized bed for the high temperature oxidation of propane with oxygen. Considerations of flow rates, catalyst inventories, heat evolution and heat transfer surface per volume of reactor made a small diameter reactor desirable. In fluidization, superficial velocities of the order of 0.5 to 1.0 feet per second are required. A smaller diameter reactor requires smaller amounts of reactant gases. Blending of small batches to obtain large amounts of prepared catalysts would be unnecessary for a small reactor. Heat can be distributed more rapidly in a small bed, and geometry makes more surface per unit volume available for heat transfer in small sized reactors. A one inch pipe was considered a convenient size for the reactor.

However, it is very difficult to get good fluidization in pipes of less than two inches in diameter. In smaller

diameter pipes the bed was subject to slugging and uneven distribution of gas and solids. Several methods to break up the gas slugs were tried. The most successful method found used a series of horizontal plates with holes in them mounted at equal intervals on a central shaft which was given an up and down motion by an eccentric drive.

A glass apparatus was built so that visual observations of the bed characteristics could be made. Figure 1 is a flow diagram and Figure 2 is a photograph of the final model. Air flow was measured by a rotameter, and its temperature and pressure were also measured. The air then passed into two surge tanks. These tanks were necessary because the plates, moving up and down in the reactor acted as a plunger which alternately increased and decreased the pressure on the inlet line, causing a pulsation in the rotameter. These pulsations were removed by the inclusion of the surge tanks.

The gas leaving the surge tanks passed into the lower section of the fluidization apparatus, where the temperature and pressure were again measured. This section was packed with four inches of copper wool. A 200 mesh screen separated the packed section from the fluidization chamber. The enlargement section above the chamber settled out some of the solids. The gas was taken out through a tee, past a thermometer and pressure tap and into a cyclone separator

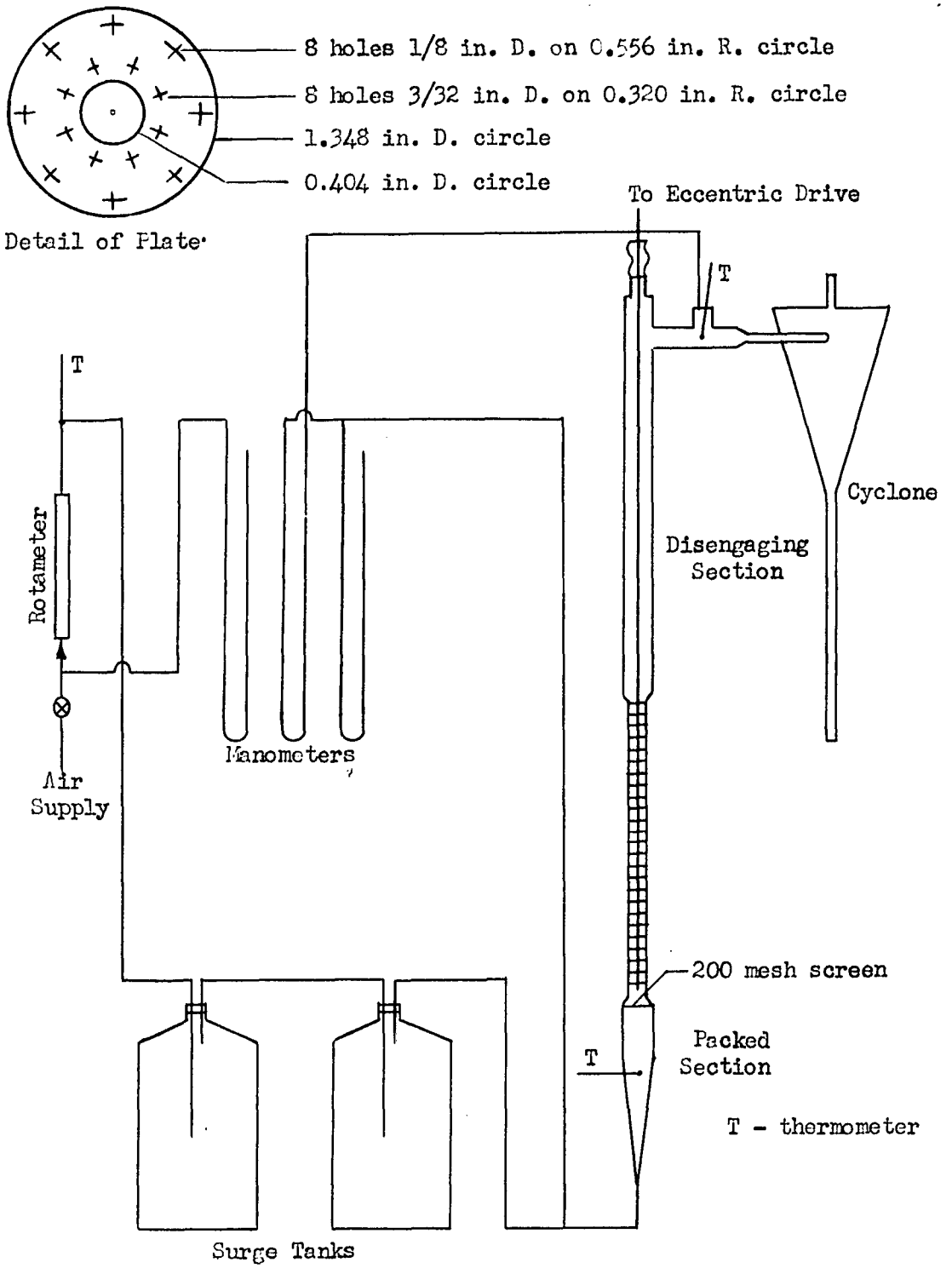

Figure 1. Flow Diagram of Glass Fluidization Equipment

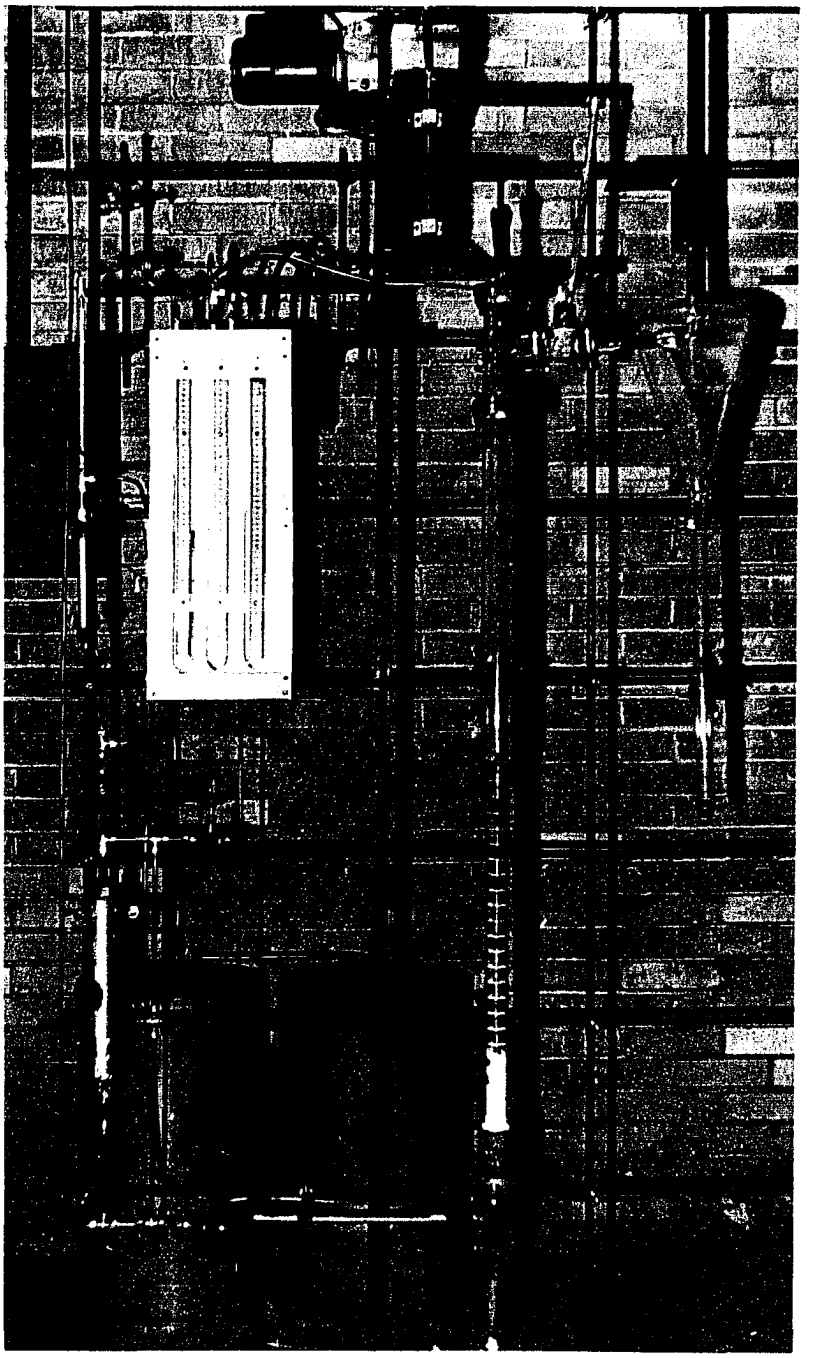

Figure 2. Glass Fluidization Equipment

where any remaining catalyst was removed.

The mechanical agitator consisted of 25 plates mounted one inch apart on a central shaft of one eighth inch pipe. Each plate cut from 0.015 inch stainless steel had sixteen holes as shown by the detail drawing in Figure 1. The plate and shaft assembly was given an up and down motion by an eccentric driven by a Graham motor with speed continuously variable between 20 and 180 rpm. The length of the stroke could be varied from one quarter to one inch in quarter inch increments.

This apparatus gave a good distribution of the catalyst in the gas with no slugging. The plates broke up any slugs that started to form. The catalyst extended itself over several plates in what appeared to be a series of small fluidized beds on top of each plate. When no vertical motion was given to the plate assembly, the catalyst tended to creep up to the upper plates, leaving a virtually empty section around the lower plates.

Tests were made to study catalyst circulation within the bed by charging layers of colored and uncolored catalyst. It was found that catalyst from the top section of the banded bed reached the bottom in 30 to 40 seconds after the gas flow was started. These tests were made without the benefit of the motion of the plates since this motion could not be started until after the gas flow had begun. With

plate motion, the mixing was even more rapid. When the catalyst was not extended by means of the gas flow it formed such dense packing around the plates that they could not be moved downward.

The nature of the bed formed in this apparatus is shown by Figure 3. The holes in the plates permitted the catalyst to move both up and down as the gas passed upward through the bed. Some gas also passed between the plates and the tube walls, since the outer diameter of the plates was 1.348 in. and the inside diameter of the chamber was 37 mm. or 1.457 in. There was no sign of extensive channeling around the plates.

The results of tests made to determine the response of the bed to pulse and flow rates are shown in Table 8. These data are plotted in Figure 4. The lines shown for constant pulse rate were obtained by replotting points obtained from a cross plot of the lines originally estimated as representing the data. The original data are given on the plot. Figure 4 shows that, for a given weight of catalyst and a given flow rate, the bed height can be varied up to 20 percent by a change of pulse rate. This is a control feature which is not present in the usual fluidized bed, whose height is uniquely determined for a given flow rate. The variation of bed height for constant flow rates by means of the pulse rate is more clearly shown in Figure 5, which is a cross

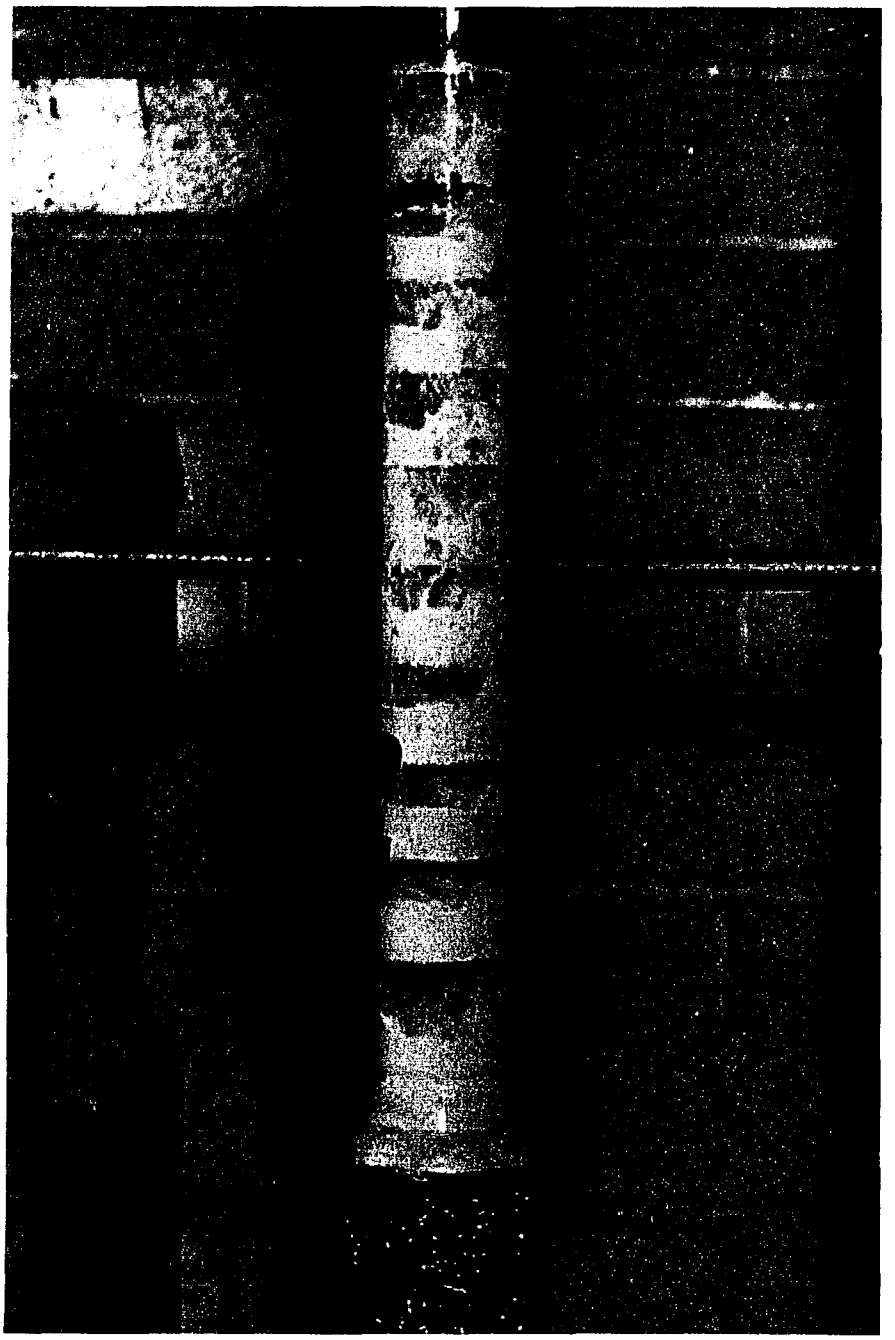

Figure 3. Bed Produced in Pulsing Plate Fluidizer

Table 8

Variation of Bed Height with Pulse and Flow Rates in Glass Apparatus[a]

Pulse rate pulses/min.	Flow rate $cm.^3/min.$[b]	Bed height in.
24	3,350	5.75
24	3,980	6.25
24	5,830	6.88
24	7,950	8.5
24	9,660	8.75
24	11,600	10.5
64	4,900	7.0
64	5,540	7.38
64	7.450	7.75
64	9,350	9.5
64	11,500	10.5
96	5,190	7.38
96	6,690	7.75
96	8,300	8.5
96	9,940	10.38
96	11,600	11.5
145	5,930	8.0
145	7,800	8.63
145	9,920	10.5
145	12,050	11.38
180	5,330	8.5
180	6,000	8.75
180	7,540	9.25
180	9,250	10.38
180	11,600	11.63

[a]Plate spacing, 1 in.; Pulse length, 0.5 in.; Catalyst type, A; Catalyst weight, 100 gm.

[b]At 14.7 psia. and 70° F.

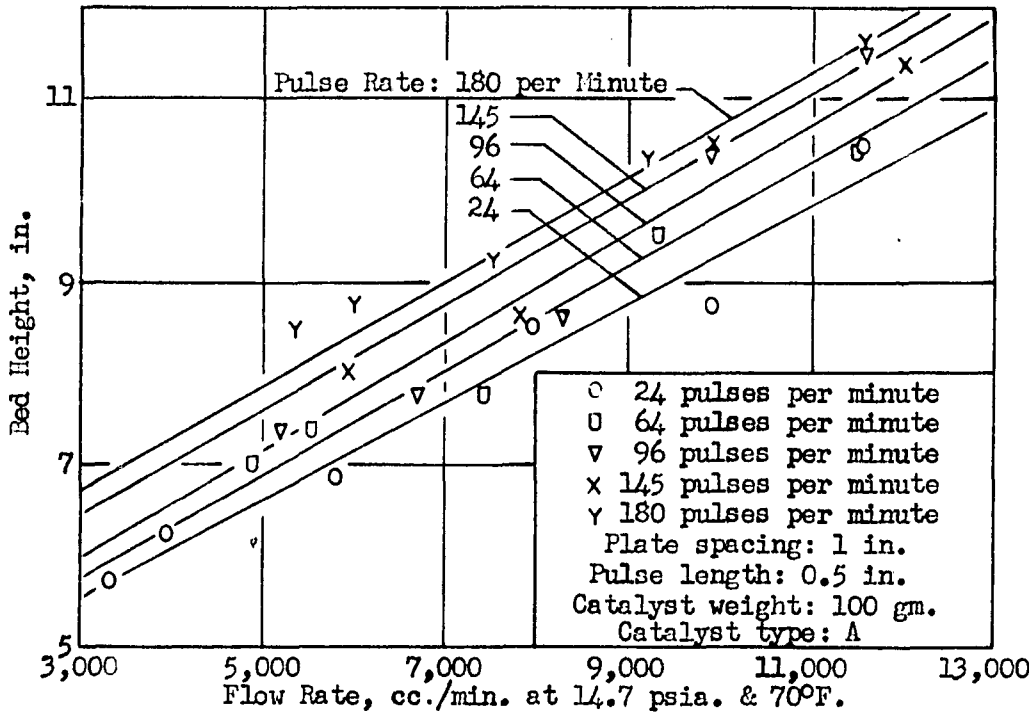

Figure 4. Variation of Bed Height with Flow Rate for Various Pulse Rates

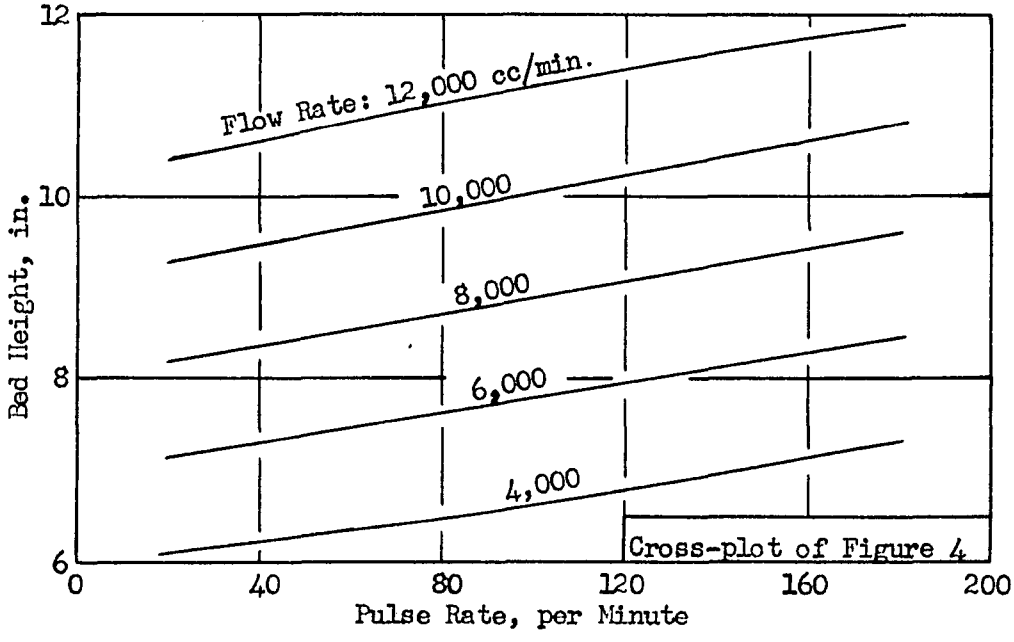

Figure 5. Variation of Bed Height with Pulse Rate for Various Flow Rates

plot of the information in Figure 4.

B. Description of Equipment

The equipment used to study the oxidation of propane provided for mixing heated, measured amounts of oxygen and propane in the presence of a fluidized catalyst at various temperatures and flow rates. The products of the reaction were then separated and analyzed.

The propane used was "natural" propane, obtained from the Matheson Company, Joliet, Illinois, guaranteed to contain at least 96% propane. Tanks containing 100 pounds of this gas were stored outside because of safety requirements. The oxygen was 99.5% oxygen obtained from the Balbach Company of Omaha, Nebraska. Both propane and oxygen cylinders were fitted with standard automatic regulators which indicated the cylinder and controlled delivery pressures.

Figure 6 is a flow diagram of the apparatus. The propane was brought in through an outside solenoid valve operated from the inside panel board. The propane and oxygen flows were measured by rotameters where the pressure and temperature of both streams were also measured. From the rotameters the gases passed separately through check valves and into electric preheaters. These heaters consisted of one eighth inch stainless steel pipe wound with B. & S. 20

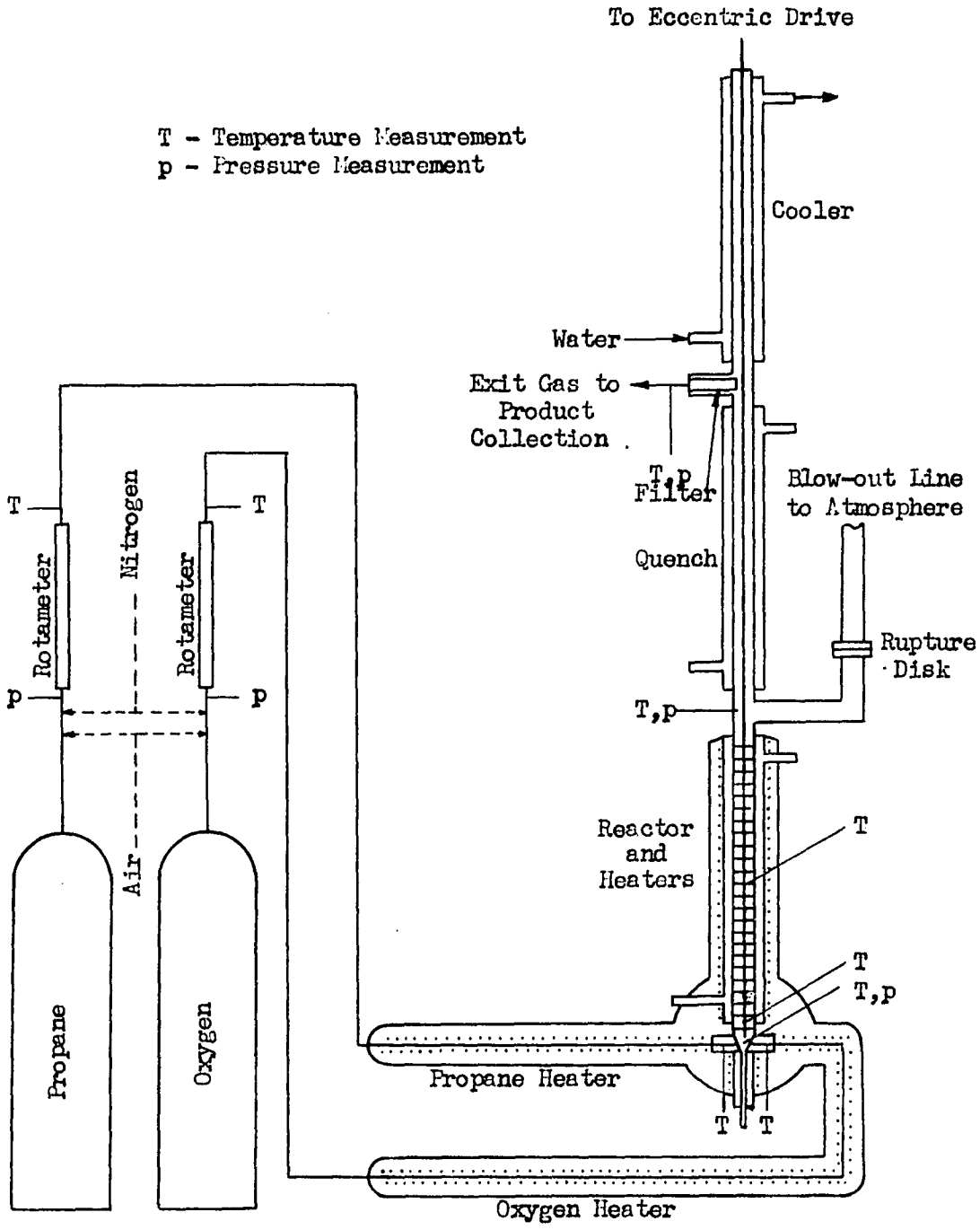

Figure 6. Equipment Flow Sheet

gauge Chromel "A" asbestos insulated resistance wire. The heaters were controlled by variable transformers. It was necessary to use copper tubing as a liner for the propane heater because stainless steel caused carbon formation which blocked the heater and cut off the gas flow. The heaters and pipes were surrounded by two inches of insulation. The oxygen and propane heaters were connected directly to the mixing flange of the reactor. A picture of the lower portion of the reactor, including the mixing flange is shown in Figure 7. The flange, one inch thick and placed at the bottom of the reactor, provided a means for introducing oxygen and propane directly into the bed from opposite sides. The propane entered from the heater on the left and the oxygen from the heater on the right. The tubes containing the leads to the thermocouples in the entrance lines can be seen extending straight down on either side of the central plug. The leads to a thermocouple inserted into the bed through the flange were in the tube extending towards the foreground of the picture and a similar tube extending from the rear was a pressure tap. The flange had a tapered hole in the center to facilitate draining of the catalyst. The whole flange and plug assembly was surrounded by an electrical heater made up of Chromel "A" resistance wire which was imbedded in the insulation surrounding it. It was found that the best way to seal the thermocouple leads

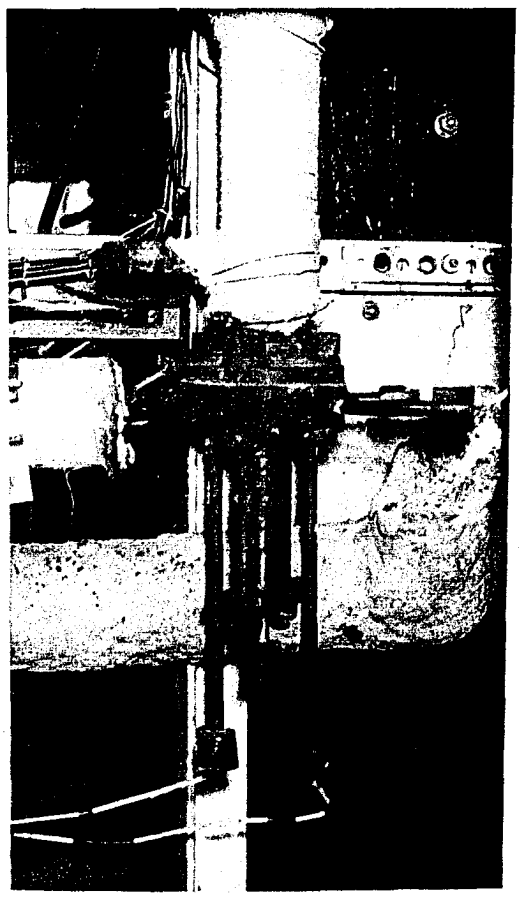

Figure 7. Bare Mixing Flange

was to enclose them in steel tubing which was welded to the flange and to extend the tubing far enough from the heaters and insulation so that it was cool enough to use a rubber stopper for a seal. The catalyst drain was sealed in a similar manner.

The reactor consisted of a two foot section of one and one quarter inch stainless steel pipe inside a two inch pipe which was fitted to act as a cooling jacket. The scale of the reaction was never large enough to require cooling and heaters were required to maintain the temperature of this large mass of metal. Three electrical heaters made of Chromel "A" resistance wire and controlled by variable transformers were placed on the reactor. The whole assembly was then covered with insulation.

A plate assembly mounted on a one eighth inch stainless steel pipe with plates at one inch intervals which exactly duplicated that of the glass apparatus was placed inside the reactor. Inside the shaft was an assembly of two thermocouples placed twelve inches apart which could be moved up and down within the shaft, even while it was in motion. By moving these thermocouples twelve inches, a full two foot temperature profile within the reactor could be obtained. The plate assembly was driven from the top by a one third horsepower motor which was connected to the eccentric driving the shaft assembly through a set of four pulleys, two

of which were variable pitched. By setting the pitch of these special pulleys the speed of pulsation could be varied from about 60 rpm. to 350 rpm.

The gases were taken off from the top of a quench section which was installed immediately above the reactor to cool the reaction products. The cooler was placed above the quench sections to give additional cooling for any gases coming in contact with the rubber seal between the apparatus and the moving shaft.

Between the reactor and quench sections a one and a quarter inch pipe led to a rupture disk with the disk set to blow at approximately 10 pounds per square inch pressure. Before leaving the quench section the gas passed through a filter to remove any entrained catalyst. The filter was made up of five layers of cloth on a screen frame and was sealed to the quench section by rubber tubing fastened with hose clamps. This made removal of the filter easy for inspection or addition of catalyst. It was later found that the quench section was actually acting as a condenser for much of the products formed so coolant flow in the jacket was stopped and a glass heating tape wrapped around it so that the gases left the quench section at a temperature of 140° F.

Figure 8 shows the product collection apparatus. After the gas left the filter it passed through a glass water-

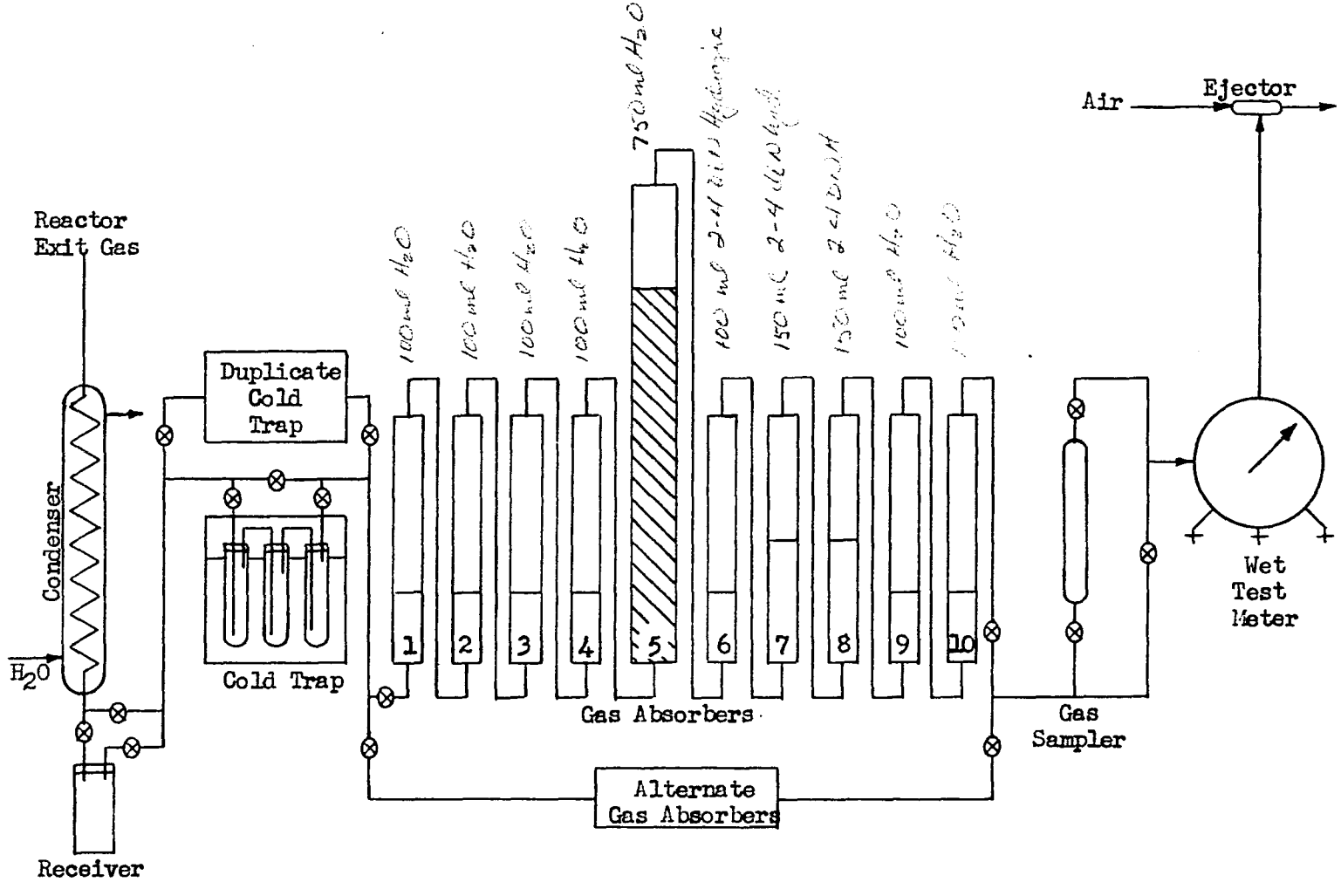

Figure 8. Product Collection Flow Sheet

cooled spiral condenser and then into a cold trap. The cold trap consisted of three rubber-stoppered 200 x 35 mm. test tubes inserted in a dry ice-trichloroethylene bath to obtain a reduced temperature. The condensibles were removed in these first two pieces of apparatus.

The gas then passed through a series of ten gas absorbers to remove any further products. Nine of the absorbers were made from 16 inch lengths of 41 mm. glass tubing with rubber stoppers in both ends. Number five absorber was a four foot section of 70 mm. glass tubing which was packed to a height of 35 inches with 7/16 inch ceramic balls. The first four and last two absorbers each contained 100 ml. of water. Number five was filled with 750 ml. of water. Absorbers seven and eight each contained 150 ml. of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 N. hydrochloric acid, while absorber six was charged with 100 ml. of the same solution. The absorbers and cold trap rubber stoppers were fitted with devices to hold the rubber stoppers in place under the slight pressures which were developed.

The gas left the absorbers and flowed through a gas sampling tube and then to a wet test meter. The metered gas was then dispersed into the outside atmosphere by means of an air ejector which also provided a vacuum in the later stages of the apparatus. The condenser product receiver,

the cold trap and the absorbing train were provided with alternate paths for the gas so that timed collection of products could be made. The absorption train, gas sampling tube and the wet test meter can be seen in Figure 9. Glass stopcocks were used to rapidly shift the gas from the run path to the bypass.

An attempt was made to centralize controls on a panel board. Flow meters, flow control valves, pressure manometers and heater controls were centered there. Eight of the thermocouple readings were taken and recorded on a Brown Electronik recording potentiometer, shown above the absorbing train in Figure 9.

The range of variables that could be studied was limited by the equipment. The rotameters put an effective limit on the flow rate of about 7,000 cc. per minute, measured at 70° F. and 14.7 psia. Flow rates from this value down to 3,000 cc. per minute were studied, so that a two-fold range of flow rates was included.

At normal temperatures, the explosive limit of oxygen in propane is about 50% (19). To be certain that this limit was not exceeded, it was decided to keep the oxygen concentration in the feed at 35% or below. Oxygen concentrations of 10, 20 and 30% were investigated. Although temperatures of 1,450° F. were encountered during the experiments the equipment was not designed to operate continuously above 1,000° F.

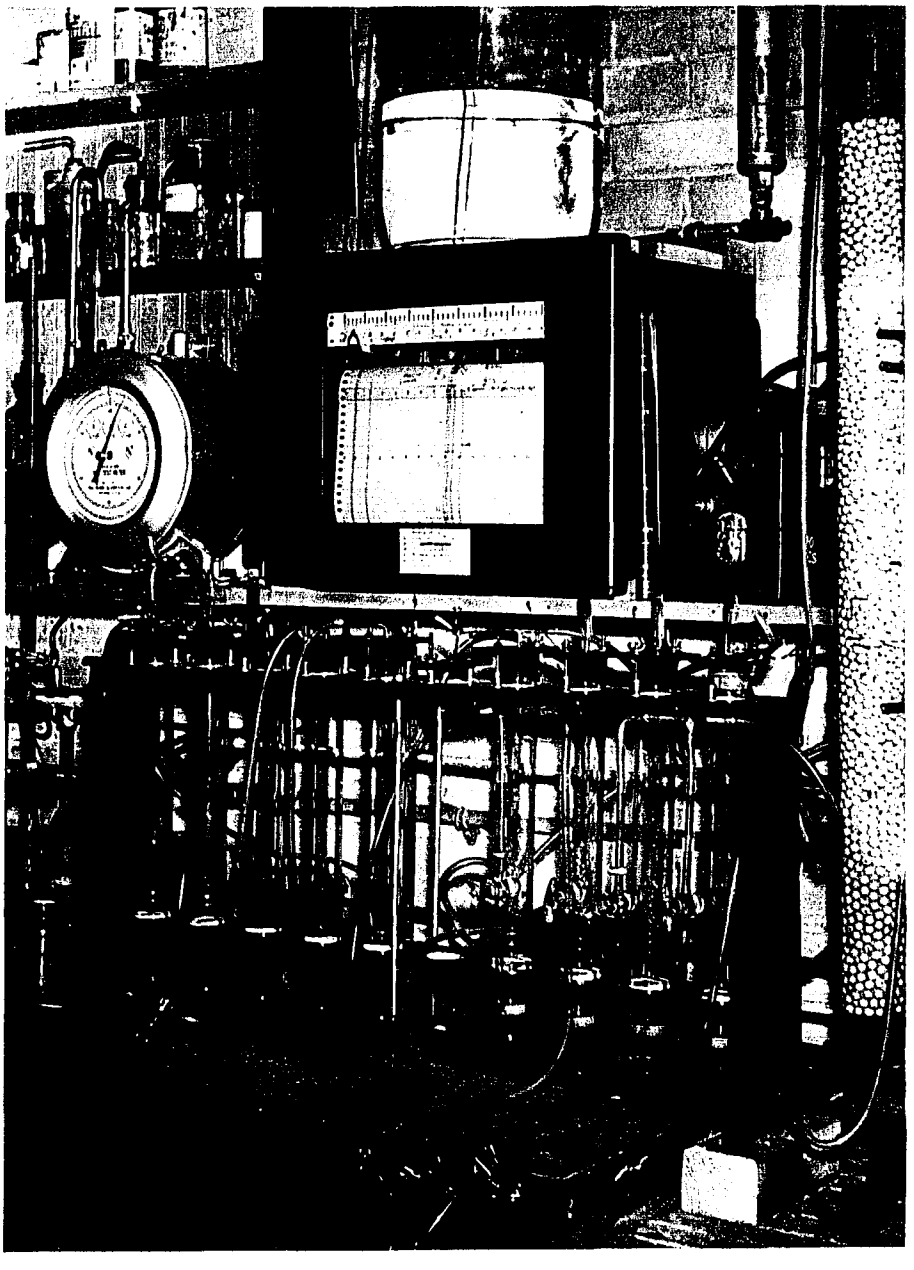

Figure 9. Absorption Train

Explosion and fire are ever present dangers when working with hydrocarbon gases, and safety provision were of paramount importance. The propane was stored outside and its flow could be stopped from the inside by means of a solenoid valve. The apparatus was built in a separate laboratory. The equipment was provided with a rupture disk, vented to the outside. During operation an exhaust fan placed outside removed gases through a line, fitted with a flame arrester, placed near the floor so that any escaping propane, which is heavier than air, would be removed. Warning lights and signs, placed near all the entrances and inside the laboratory, cautioned against smoking or flames in the vicinity during operation. Tests were made with an explosion meter to discover any leaks. The propane and oxygen lines were both fitted to nitrogen and air supplies so that these gases could be used in warm-up and shut-down periods and so that the lines and equipment could be purged of explosive gases when necessary.

C. Operating Procedure

The procedures developed for making a run or a series of runs required two operators. The catalyst was charged into the empty reactor through the filter opening. The filter was replaced and an air flow was started through

both lines. All heaters were turned on to their maximum settings. The temperature recorder was turned on at the same time. As the temperatures neared the desired operating level the variable transformers were adjusted to keep the temperatures near this level. This warming up period required from two to four hours, depending on the temperature of the run. Nitrogen was then introduced into both lines to purge all the equipment of air to avoid explosive mixtures when the propane was introduced. After the nitrogen had been flowing at least ten minutes the propane was introduced, causing a definite temperature drop because of the different specific heat of the propane. The heater settings were adjusted to counteract this variation and the pulsating plate assembly was started. During the runs the oxygen flow was begun from five to ten minutes after the propane flow was started. When the oxygen flow was begun the bed temperatures immediately increased due to heat of reaction. The temperatures were brought back to the desired levels by adjustment of the heaters.

Liquid product appeared in the condenser about four minutes after the oxygen flow was begun. Steady state conditions, indicated by lining out of the temperatures on the recorder and the steady production of liquid product, requiring about an hour to attain, were reached before a timed collection of the product was begun. The pressure

and flow readings were noted prior to the beginning of the timed collection and the flows adjusted to the desired conditions. Up to this time the gases had been passing through the alternate cold trap and absorbing columns.

A stop watch was started and the wet test meter read at the start of a timed collection of products. One of the operators then immediately switched the gas flow to the prepared gas absorbers and cold trap. The other replaced the condenser product receiver. The whole switching process could be accomplished in less than 20 seconds. Thirty minute product collections were made. During this time enough product could be collected to characterize the run and if the conditions of operation were not conducive to the production of any product, a thirty minute run would also reveal this.

Immediately after the start of the run a complete set of readings was taken. All of the pressures and temperatures were read. This included a check of all of the temperatures indicated on the continuous recorder by means of a Leeds and Northrup No. 8662 potentiometer. A complete list of the data taken during a run is contained in Appendix B. The variable transformer settings and the heater current were recorded also. Efforts were made during the run to keep the flows and pressures constant. The exit gas was run through the gas sampling tube for at least ten minutes to

obtain a representative sample. Another set of readings was made near the end of the run and recorded. Values reported are averages of readings taken.

After thirty minutes had elapsed the wet test meter reading was noted and the gas switched back to the alternate absorbers and cold trap and the condenser product receiver replaced in the same order as at the beginning of the run. Then, if another run was to be made in the same series, adjustments were made to the heater and flow settings so that the new steady state could be attained as soon as possible. While steady state was being reached under the new conditions the liquid product was collected. This involved the removal of the three cold trap containers and the draining of the first five absorbers. This material was combined with the measured condenser product. All absorbers, the cold trap containers and the condenser product receiver were thoroughly rinsed and the washings combined with the original product. This liquid was then made up to 2,000 ml. in a volumetric flask. The water from absorbers nine and ten was first drained and a qualitative test made for aldehydes and ketones to determine if any of these materials had not been retained in the first eight absorbers. If the test proved negative the solutions were discarded. If it proved positive they were added to the liquid product. The 2,4-dinitrophenylhydrazine precipitate was collected from

absorbers six, seven and eight. The liquid product collection required one hour.

When the last run in the series had been made, nitrogen was switched into the oxygen line first and later into the propane line. All heaters were turned off except the glass tape heater on the quench section which was left on to prevent any condensation of product during the cooling period. After nitrogen had been flowing for at least ten minutes, an air flow in the gas lines was maintained while the apparatus was being cooled. When the temperatures were low enough the gas flow was stopped and the catalyst drain plug removed in order to collect the remaining catalyst, which was then weighed.

The gas sample taken during the run was analyzed by a standard Orsat analysis which gave the volume percentages of carbon dioxide, unsaturated hydrocarbons, oxygen and carbon monoxide by chemical absorption and a term for propane and others by difference.

The liquids were analyzed for content of acid, aldehydes and ketones, and alcohols by volumetric analyses. These general classifications of useful products were of interest simply to indicate the scale of the conversion accomplished. Once high conversions were attained, more detailed analyses would be made. The details of the gas and liquid analyses are found in Appendix A.

Calculation based on the data and the analyses were made to determine the results of the run. The calculations were designed to determine how much of the oxygen, the limiting reactant, had been converted to each of the products and from this to determine effects of catalyst, flow rate, temperature and feed composition. The detailed procedure followed during each calculation is found in Appendix B.

D. Experimental Results

Runs using four catalysts, designated as A, B, C and D were made. Catalyst A was Celite, a diatomaceous earth prepared by Johns Manville Company. Catalyst B was catalyst A coated with copper oxide. Catalyst C was made up of a mixture of 50% catalyst A and 50% catalyst B. Catalyst D contained 75% catalyst B and 25% catalyst A. A detailed description of the catalysts and their preparation is given in Appendix C.

Table 9 is a compilation of the conditions and results of all of the runs reported. The number of the run and the type of catalyst used is given at the head of each column. Item 2 was used to designate the run temperature. Items 4 and 5 do not include the inactive catalyst contained in the catalyst drain line.

Item	Run number and catalyst used	34-A	35-A	36-A	37-A	38-A	39-A
	RUN CONDITIONS						
	Temperatures, °F.						
1	Mixed gases at reactor bottom	950	954	944	965	956	956
2	1 in. above bottom	953	953	956	967	958	955
3	13 in. above bottom	cyclic	897	1001	925	965	939
	Catalyst						
4	Weight charged, gm.	100			100	100	
5	Weight recovered, gm.			87	129		100
6	Reactor pressure, in. Hg., abs.	33.87	34.93	34.83	36.24	34.09	35.61
	Feed						
7	Rate, cm.^{3}/min. at 14.7 psia. and 70° F.	3229	3282	3239	3398	3128	3473
8	Oxygen, volume %	30.1	29.5	29.4	30.5	10.2	20.4
9	Dry exit gas, mg. moles	2877	2478	2808	3602	2592	3308
	RUN RESULTS						
	Dry exit gas analysis, volume %						
10	Carbon Dioxide	3.7	3.3	2.9	2.9	0.5	2.1
11	Unsaturated hydrocarbons	26.5	27.0	27.6	26.6	6.0	21.1
12	Oxygen	1.4	1.0	0.9	2.6	3.0	2.1
13	Carbon monoxide	10.1	10.4	10.7	10.7	0.4	5.2
14	Propane and others, by difference	58.3	58.3	57.9	57.2	90.1	69.5
	Weight of liquid products, mg. moles						
15	Acids	0	0	0	0	0	0
16	Alcohols	3.57	3.57	4.82	8.03	1.37	11.24
17	Aldehydes and ketones	37.79	53.72	58.36	64.3	9.76	49.95
18	Total useful products	41.36	57.29	63.18	72.33	11.13	61.19
	Distribution of oxygen fed, %						
19	Carbon dioxide	8.8	6.8	6.9	8.1	3.3	7.9
20	Oxygen	3.3	1.0	2.1	7.3	19.6	7.9
21	Carbon monoxide	12.1	10.7	12.7	14.9	1.3	9.8
22	Acids	0	0	0	0	0	0
23	Alcohols	0.15	0.15	0.20	0.31	0.17	0.64
24	Aldehydes and ketones	1.56	2.23	2.47	2.49	1.23	2.83
25	Total useful products	1.71	2.38	2.67	2.80	1.40	3.47
26	Total in dry measured products	25.9	20.9	24.4	33.1	25.5	29.0
	Total, including H_2O of reaction						
27	Maximum	80.9	62.6	81.2	98.0	48.9	89.6
28	Minimum	69.2	51.7	68.5	83.8	41.4	74.1
29	Accountability of carbon fed, maximum %	93.2	79.5	91.2	111.0	71.9	91.7

Table 9

Experimental Results

	38-A	39-A	40-A	41-A	42-A	43-A	44-B	45-B	46-B	49-B	50-C	51-C	52-C	53-C
	956	956	951	960	833	899	497	650	804	427	917	942	843	844
	958	955	967	984	828	907	520	662	815	823	901	945	858	849
	965	939	948	958	844	893	500	642	760	675	898	930	854	856
	100		100		100		105		100	100	100		100	
		100		100		81		106	90	76		74		91
4	34.09	35.61	36.93	40.47	38.30	40.72	39.95	41.03	36.56	46.68	43.00	45.98	40.16	35.64
	3128	3473	4901	6112	6019	6273	6399	6249	7237	6279	6182	6685	6150	4744
	10.2	20.4	18.2	20.6	19.8	19.9	19.5	19.6	19.4	19.1	10.1	9.6	10.5	10.2
	2592	3308	4109	5646	4916	5358			7009	6767	6823	7435	7559	5604
	0.5	2.1	1.9	1.2	0.2	1.1			0.2	6.8	2.6	3.0	0.8	0.6
	6.0	21.1	17.5	23.0	1.6	0.4			0.4	0.2	7.8	9.4	0.5	0.4
	3.0	2.1	1.4	1.5	14.5	11.9			20.2	5.2	2.6	0.9	9.5	8.9
	0.4	5.2	3.2	4.9	0.3	0			1.7	1.1	1.0	1.4	0.1	0.1
	90.1	69.5	76.0	69.4	83.4	83.0			77.5	86.7	86.0	85.3	89.1	90.0
	0	0	0	0.77	0	0			0	0	0.74	0.37	0	0
3	1.37	11.24	10.71	14.98	0	1.61			1.43	0	3.57	6.60	0	0
	9.76	49.95	57.72	97.89	5.99	20.48			0.37	1.60	31.87	47.18	3.03	2.85
3	11.13	61.19	68.43	113.64	5.99	22.09			1.80	1.60	36.18	54.15	3.03	2.85
	3.3	7.9	7.1	4.3	0.8	3.8			0.8	30.8	22.9	27.9	7.5	5.9
	19.6	7.9	5.2	5.4	59.0	41.1			81.2	23.6	22.9	8.4	89.3	87.3
	1.3	9.8	5.9	8.9	0.6	0			3.4	2.5	4.4	6.5	0.5	0.5
	0	0	0	0.05	0	0			0	0	0.10	0.05	0	0
1	0.17	0.64	0.48	0.48	0	0.05			0.04	0	0.23	0.41	0	0
9	1.23	2.83	2.61	3.13	0.20	0.66			0.01	0.05	2.06	2.95	0.19	0.24
0	1.40	3.47	3.09	3.66	0.20	0.71			0.05	0.05	2.39	3.41	0.19	0.24
	25.5	29.0	21.3	22.3	60.6	45.6			85.5	56.9	52.6	46.2	97.5	93.9
	48.9	89.6	65.0	75.9	65.5	55.7			91.4	81.3	110.1	120.2	105.6	100.7
	41.4	74.1	52.3	59.5	64.2	52.9			90.7	81.1	97.1	103.3	104.8	99.9
	71.9	91.7	79.9	90.3	85.5	75.3			76.0	93.2	94.4	96.0	99.4	101.0

No product observed; no samples taken

No product observed; no samples taken

45-B	46-B	49-B	50-C	51-C	52-C	53-C	54-C	55-C	56-C	57-B	58-B	59-D	Item
650	804	427	917	942	843	844	835	830	828	835	858	820	1
662	815	823	901	945	858	849	858	847	853	850	957	849	2
642	760	675	898	930	854	856	848	850	861	840	952	914	3
	100	100	100		100		100			100		100	4
106	90	76		74		91			117		80	75	5
41.03	36.56	46.68	43.00	45.98	40.16	35.64	33.67	37.16	40.97	34.84	40.51	39.15	6
6249	7237	6279	6182	6685	6150	4744	3157	4867	4098	4714	4751	4693	7
19.6	19.4	19.1	10.1	9.6	10.5	10.2	9.0	20.0	29.3	19.2	20.0	19.3	8
	7009	6767	6823	7435	7559	5604	3651	5694	5510	5583	5557	5658	9
	0.2	6.8	2.6	3.0	0.8	0.6	1.0	0.6	1.5	0.5	6.2	4.5	10
	0.4	0.2	7.8	9.4	0.5	0.4	0.6	1.1	2.0	0	8.9	18.8	11
	20.2	5.2	2.6	0.9	9.5	8.9	7.0	17.8	25.5	18.0	4.5	1.7	12
	1.7	1.1	1.0	1.4	0.1	0.1	0	0.3	1.0	0.4	4.0	4.9	13
	77.5	86.7	86.0	85.3	89.1	90.0	91.4	80.2	70.0	81.1	76.4	70.1	14
	0	0	0.74	0.37	0	0	0	0	0	0	0.74	0.74	15
	1.43	0	3.57	6.60	0	0	0	1.78	3.57	0	7.14	4.28	16
	0.37	1.60	31.87	47.18	3.03	2.85	0.83	3.77	14.25	0.77	32.71	46.68	17
	1.80	1.60	36.18	54.15	3.03	2.85	0.83	5.55	17.82	0.77	40.59	51.70	18
	0.8	30.8	22.9	27.9	7.5	5.9	10.3	2.8	5.6	2.5	29.2	22.7	19
	81.2	23.6	22.9	8.4	89.3	87.3	72.4	83.9	94.2	89.4	21.2	8.6	20
	3.4	2.5	4.4	6.5	0.5	0.5	0	0.7	1.9	1.0	9.4	12.3	21
	0	0	0.10	0.05	0	0	0	0	0	0	0.06	0.07	22
	0.04	0	0.23	0.41	0	0	0	0.07	0.12	0	0.30	0.19	23
	0.01	0.05	2.06	2.95	0.19	0.24	0.12	0.16	0.48	0.03	1.38	2.08	24
	0.05	0.05	2.39	3.41	0.19	0.24	0.12	0.23	0.60	0.03	1.74	2.33	25
	85.5	56.9	52.6	46.2	97.5	93.9	82.7	87.7	102.2	92.9	61.4	45.9	26
	91.4	81.3	110.1	120.2	105.6	100.7	93.0	93.3	112.6	95.9	116.3	126.9	27
	90.7	81.1	97.1	103.3	104.8	99.9	91.9	92.2	110.9	95.9	108.1	109.5	28
	76.0	93.2	94.4	96.0	99.4	101.0	94.5	96.1	111.9	96.0	105.3	111.7	29

No product observed; no samples taken

The volume of dry exit gas, stripped of all liquid products was used to determine item 9. Items 10 through 14 give the contents of this gas. The amounts of the useful products, defined as acids, alcohols, and aldehydes and ketones are found in items 15, 16 and 17 with the total in item 18.

Items 19 through 28 are an indication of what happened to the oxygen fed. Item 25 is the total of items 22, 23 and 24 and has been used as the means of comparison of the runs. Item 26 is the sum of items 19 through 24 and indicates the amount of oxygen fed which has been directly measured in the reactor exit gas. Items 27 and 28 include item 26 plus the maximum and minimum amounts of the oxygen in the hypothetical water of reaction possibly associated with the various products measured.

Item 29 gives the accountability of the carbon if all products measured were assumed to contain the maximum possible carbon.

V. DISCUSSION

A total of 59 runs was made on the equipment. Runs one through 34 were necessary to perfect the equipment and the product collection apparatus and to develop operating procedures. During these runs it was found that a temperature of 800° F. was necessary, even with the catalyst, to effect any conversion to useful oxygenated products. A tendency for the temperature above the catalyst to increase in an uncontrollable manner was also noted when the bed was operating at 950° F. It was impossible to maintain the temperature above the bed at 950° F. but it could be kept at 900° or 1,000° F. Runs 34, 35 and 36 were made to determine the effect of this temperature. Runs 37 through 43 were made to determine the effect of temperature, flow rate and feed composition on conversion while using catalyst A.

Runs 44 through 46 were made to study the effect of catalyst B at 500° F. and 800° F. Runs 47, 48 and 49 were made to test catalyst B at 875° F. but the temperatures could not be controlled. Accidents prevented the taking of observations and products during runs 47 and 48 so they are not reported. Run 49 was only partially successful, so a new catalyst, C, was tried. Runs 50 through 56 were a

series to evaluate the effects of temperature, flow rate and feed composition on conversion in the presence of catalyst C. Runs 57, 58 and 59 were made to study the effect of catalyst composition on the yield.

Temperature was the variable which had most effect on the conversion of oxygen to useful products. Very little conversion was noted with any of the catalysts below 800° F. The effect of temperature on conversion is shown by runs 41, 42 and 43 for catalyst A and by runs 50, 51 and 52 for catalyst C. Figure 10 is a plot of items 3 and 25 in Table 9, and shows that the yield of useful products increased with temperature for both catalysts A and C. It will be noted that the points were not taken at exactly the same conditions of flow rate and composition and are not strictly comparable. Neither curve appears to have reached a maximum, indicating that increasing the temperature would probably increase the yield of useful products.

The experience with the equipment verified the temperature control exercised by a fluidized bed, but showed that this control was subject to limitations. If the propane and oxygen, heated to the desired reaction temperature, were mixed before they were in the presence of the catalyst they would react immediately and the temperature at the point of mixing would be very high. Mixing in the presence of the catalyst eliminated this problem. It was also impossible

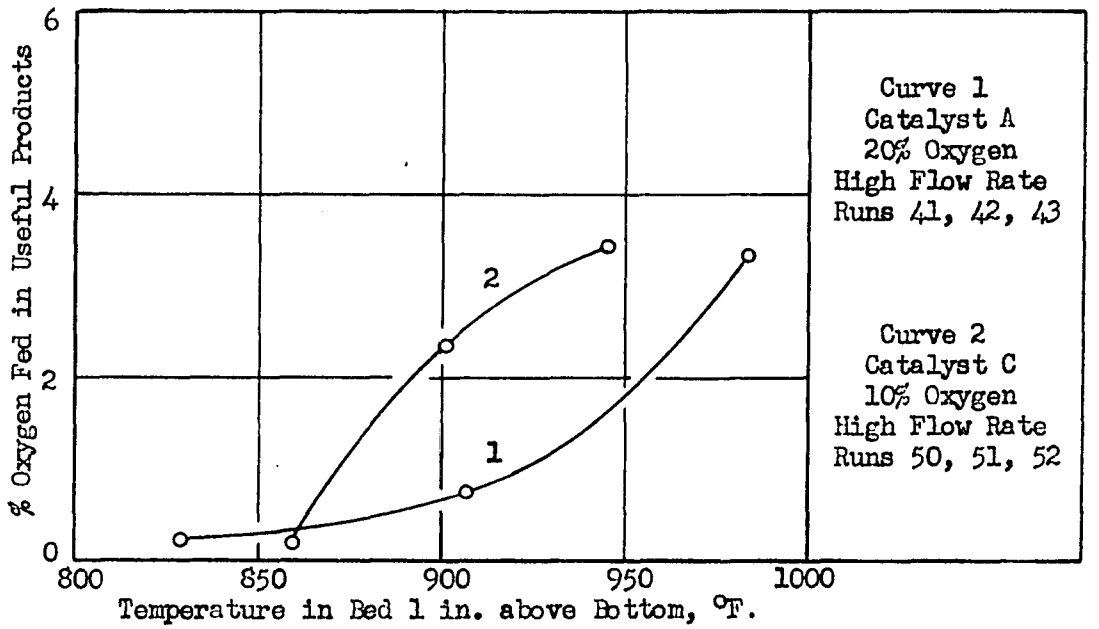

Figure 10. Effect of Temperature on Conversion

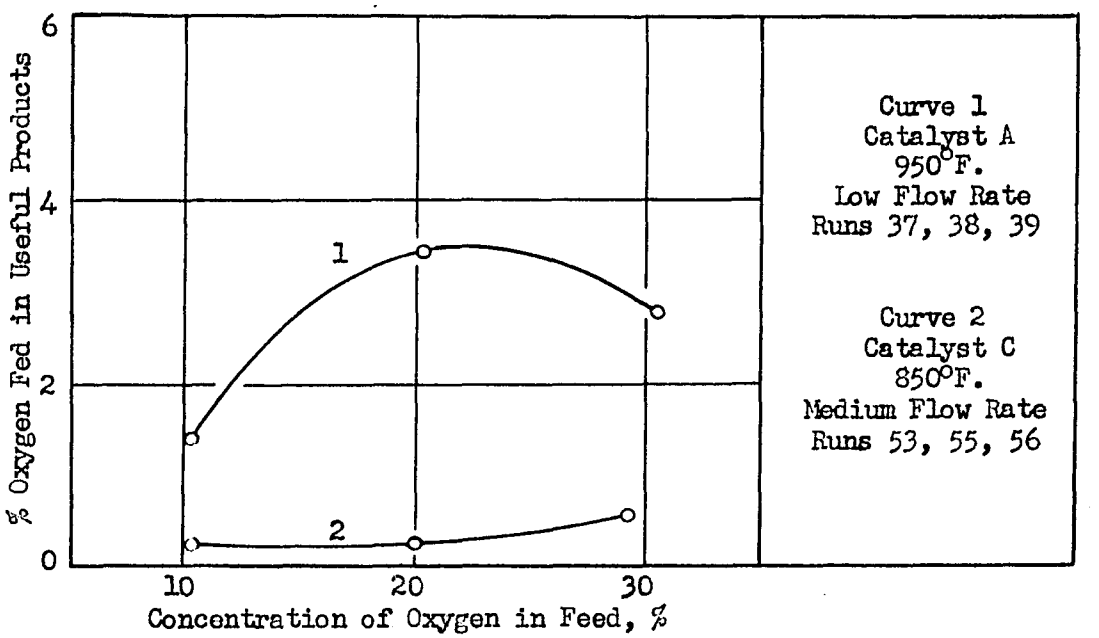

Figure 11. Effect of Feed Composition on Conversion

to make blank runs with no catalyst because the reactor temperature could not be controlled. There were limits to the ability of the bed to control the temperature. With catalyst A it was noted that the temperature 13 in. above the bottom of the bed had a tendency to vary in an uncontrollable fashion at an operating temperature of 950° F. This thermocouple was normally above the level of the catalyst and it is probable that the gases leaving the influence of the bed and still containing free oxygen behaved as if they were just coming into contact with each other at this high temperature with a resultant hot spot. Efforts to keep this temperature at 950° F. were unsuccessful, resulting in a cycling temperature above and below the desired temperature. A somewhat strange development was the ability to control this temperature at 900° or 1,000° F. Runs 34, 35 and 36 were made to study the effect of these temperatures and show from item 25 in Table 9 that it is better to run with the temperature just above the bed at 1,000° F. in run 36 than at 900° F. in run 35 with both giving better results than the cycling temperature of run 34.

Catalyst B employed copper oxide because of its oxidation potentialities. It promoted product formation at temperatures below those found necessary for catalyst A. However, when temperatures of 875° F. were employed the temperatures within the bed could not be controlled. This

was probably due to the powerful effect of the copper oxide which forced the reaction to proceed rapidly at this temperature despite the effect of the fluid bed. This action was noted in runs 47 and 48. In run 49 an attempt was made to control the bed temperature by feeding relatively cool reactants and using the heat of reaction to raise their temperature to the reaction temperature. This was partially successful but the control was still poor.

When catalyst C was used, the bed temperatures could not be controlled at temperatures of 900° F. and 20% oxygen concentration in the feed. When the oxygen content was reduced to 10%, thus reducing the total possible reactant material and the heat of reaction the temperature could be controlled, indicating that the bed could dissipate this reduced amount of heat.

The effect of oxygen concentration in the feed was shown by runs 37, 38 and 39 for catalyst A and runs 53, 55 and 56 for catalyst C. Figure 11 is a plot of items 8 and 25 from Table 9 for these runs. The plot for catalyst A indicates that a maximum conversion of oxygen to useful products was obtained with a 20% concentration of oxygen in the feed. With catalyst C there was not too much variation of conversion with concentration, although the 30% point was slightly higher than the others. The individual catalysts were run at different temperatures so that the

two curves obtained are not strictly comparable.

Runs 39, 40 and 41 were made to show the effect of flow rate on conversion for catalyst A and runs 52, 53 and 54 for catalyst C. Items 7 and 25 from Table 9 are plotted in Figure 12 for the two catalysts. Both of these curves show that flow rate does not have much effect on conversion. There is a minimum in the curve for catalyst A at medium flow rates but it is not too pronounced. The slight maximum shown for catalyst C at the medium rate is not marked enough to conclude that this is the best flow rate. Again the two curves are not strictly comparable because of different temperatures and feed compositions.

Catalyst A was effective in the control of temperatures up to 950° F. with oxygen concentrations in the feed of up to 30%. Catalyst B was made of copper oxide coated on catalyst A to get a catalyst with stronger oxidation power, and showed better results because some product was found at 800° F. in run 46 whereas no product was found with catalyst A at this temperature. Catalyst B caused uncontrollable temperatures at lower temperatures than catalyst A, which was also attributed to its higher oxidizing power.

Catalyst C was compounded of 50% catalyst A and 50% catalyst B to gain the temperature control of the first and the oxidizing power of the second. The result was a catalyst with characteristics somewhat between the two -- it

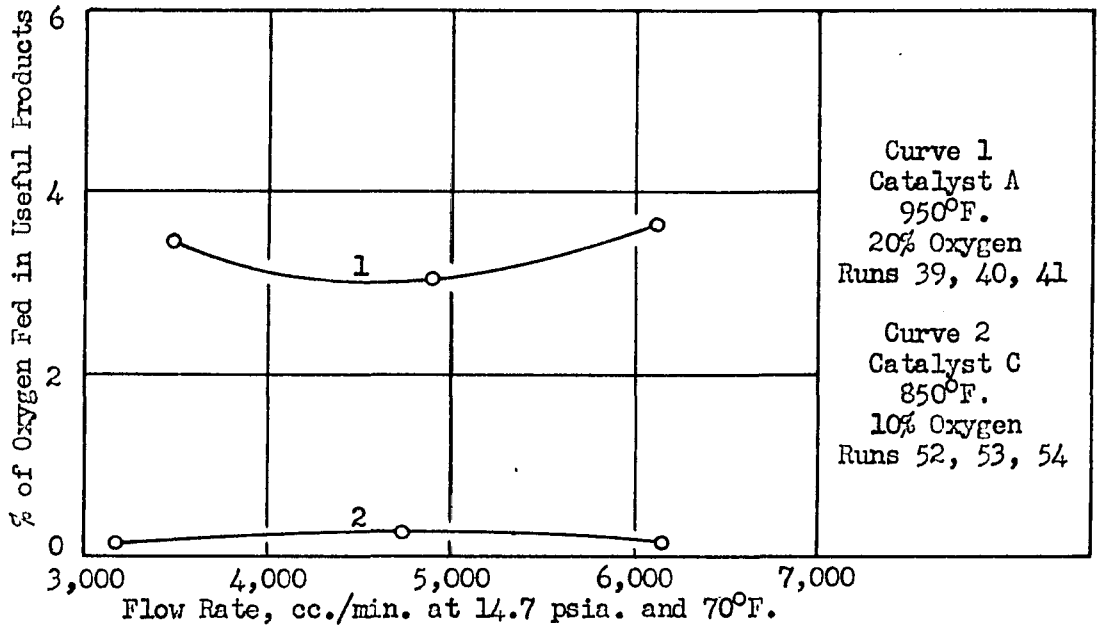

Figure 12. Effect of Flow Rate on Conversion

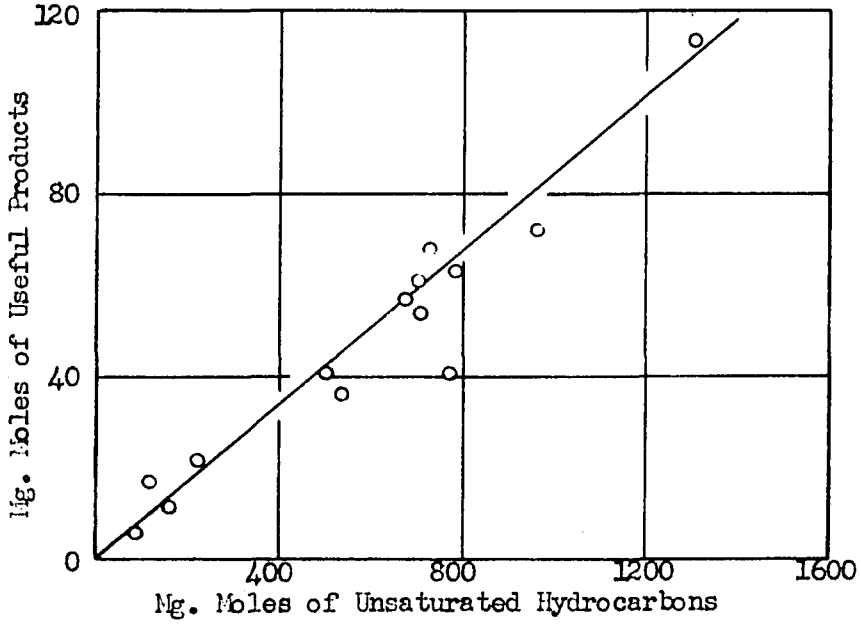

Figure 13. Relation of Unsaturated Hydrocarbons to Total Useful Products

could work at the higher temperatures of catalyst A but the oxygen concentration in the feed had to be kept at 10% at these temperatures.

Catalyst D consisted of 75% B and 25% A and was made in an effort to study the effect of catalyst composition in conjunction with B and C in runs 55, 57 and 59. This series was unsuccessful because the temperature in and above the bed could not be controlled in run 59, so no conclusion can be drawn as to the effect of the catalyst composition other than the general ones already made.

The data of Table 9 show that in all cases, there was always at least 0.9% of oxygen in the exit gas. Item 20 indicates that significant portions of the oxygen fed generally survived the reaction. This shows that the conversions obtained were not limited by the amount of reactants and that conversions conceivably could be better if only all the oxygen available were used. High concentrations of oxygen always occurred where the yield of useful products was low.

The results also show that whenever there was a significant yield of useful products there was also a relatively high concentration of unsaturated hydrocarbons in the exit gas. There is an apparent relation between these two quantities as shown by Figure 13 which is a plot of the weight of unsaturated hydrocarbons, in mg. moles, in the exit gas, (obtained by the product of items 9 and 11 in

Table 9) vs. the weight, in mg. moles, of the total useful products obtained in any run. The presence of the unsaturates is not too surprising because the Celite used as catalyst A was a commercial cracking catalyst.

The concentrations of carbon monoxide and carbon dioxide as shown by items 10 and 13 or 19 and 21 indicate that much of the oxygen was used to form these compounds from the carbon of the propane. Whether this was the result of a direct conversion or due to decomposition of useful products is not apparent from the data. High conversions to carbon monoxide and carbon dioxide usually accompanied high conversions to useful products.

The conversions reported are highest for run 41 which gave a total 3.66% of the oxygen fed converted to useful product, with 3.13% converted to aldehydes and ketones, 0.48% to alcohols and 0.05% to acids. DeWitt and Hein reported 2.95% maximum conversion under similar circumstances in an investigation of six catalysts in 105 runs (20).

The results are subject to errors introduced by the analyses. The gas analysis is accurate only to 0.1% of the total gas, which represents a much higher percentage of the component gases.

The analyses of the useful products are subject to different errors. The acid values were found by the simplest and most accurate method. The value given for the weight

of aldehydes and ketones is the sum of two values as noted in the section on analysis. The error involved by assuming that the precipitate from the 2,4-dinitrophenylhydrazine absorbers was the derivative of formaldehyde is very small. In run 51, if the precipitate had been assumed to be the derivative of acetone rather than that of formaldehyde, the total value for the weight of aldehydes and ketones would have been 97.14 instead of 97.89 and the conversion would have been reduced from 3.13 to 3.11% of the oxygen fed. This is less than 1%.

The alcohol analysis is subject to considerable error. The concentrations of alcohol found are close to the lowest values detectable by the method of analysis. The error in any reported value may be as great as 1.5 mg. moles. However, the alcohol value is only a minor portion of the total useful products and the effect of error in this term is reduced.

The conversions noted are all based on oxygen since it is the limiting reactant and an exact accounting of the oxygen content of the various classes of compounds can be made. The carbon content would be entirely dependent on analyses for all the possible compounds found. Any acid compound will always contain at least one mole of oxygen per mole of product. Alcohols, aldehydes and ketones will always contain one half mole of oxygen per mole of product, no matter what the individual compounds may be. Thus, an exact

measure of the oxygen content can be made without knowing the individual compounds whereas the carbon content cannot be known exactly unless the individual compounds are known.

Since propane was the more expensive reactant, yields based on carbon are of interest. If the products were assumed to contain the maximum possible amount of carbon, the conversion of the carbon feed for run 41 would be:

Carbon dioxide	0.4%
Unsaturated hydrocarbons	21.5
Carbon monoxide	1.5
Acids	0.01
Alcohols	0.25
Aldehydes and ketones	1.62
Total	25.29%

The maximum amount of carbon in the above products was found to be 4,583 mg. moles by calculations similar to Appendix B. If it were assumed that all of the carbon not found in those products was contained in unreacted propane in the exit gas which could be recycled to the feed, the fresh propane feed would only have to supply the 4,583 mg. moles of carbon. On the basis of this fresh carbon feed, conversions were found to be:

Carbon dioxide		1.6%
Carbon monoxide		6.0
Unsaturated hydrocarbons		85.0
Useful products		
Acids	0.05	
Alcohols	0.98	
Aldehydes and ketones	6.41	
Total useful products		7.4
Total		100.0%

Thus, 92.4% of the fresh carbon feed could be found in the useful products or in the unsaturates, with only 7.6% being converted to carbon monoxide and dioxide.

The data given for item 26, showing the amount of oxygen found in the directly measured products, does not account for a large portion of the oxygen fed when large amounts of useful products are encountered. Some of this oxygen would probably be associated with hydrogen in water.

During the formation of the oxygenated hydrocarbons from the propane some hydrogen will be liberated. There are only one or two possible products, such as methyl or ethyl alcohol, which contain more hydrogen per carbon atom than does propane. This liberated hydrogen could be present as free hydrogen, or it might be associated with either the oxygen in the form of water or with carbon in the form of other saturated hydrocarbons, methane, for example. Whenever conversion was noted there was always a large amount of liquid which was found in the condenser receiver. The amount was far too great to be only the liquid products which were measured later. Distillation of a sample revealed that there was not enough material other than water to be analyzed for in this manner. The maximum amount of hydrogen that would be available for formation of water would be obtained if it were assumed that all of the carbon from the propane converted was found in the measured dry

products and all of the hydrogen originally associated with this carbon in the propane but not found in the measured products had been converted to water. This assumption also calls for the maximum use of oxygen as associated with hydrogen.

Calculations based on this assumption were made. The amount of hydrogen available for water formation would naturally be dependent on the nature of the measured products formed from the propane. In the case of carbon dioxide and carbon monoxide, an exact relationship can be formulated and a definite amount of hydrogen is liberated when one mole of propane is converted to these products. In the case of the other products, unsaturated hydrocarbons, acids, alcohols and ketones, this amount of hydrogen cannot be exactly established since it is not known from the analysis just how much hydrogen is associated with the carbon of the product. However, the maximum and minimum amounts of hydrogen which would be available and the consequent maximum and minimum amounts of water that could be formed could be calculated by assuming that the material reported was composed of the compounds which had the least and the most hydrogen from the propane still retained in the compounds. This procedure has been followed according to the tables shown in Appendix B. Acetylene is so reactive that no compounds of this nature would likely survive the reactor. All unsaturated

hydrocarbons are thus assumed to have a double bond. The other products were assumed to be saturated.

These maximum and minimum amounts of water of reaction formed were calculated and when added to the oxygen found in the dry measured products, gave the maximum and minimum total percentages of the oxygen fed which was converted. These are the values recorded for items 27 and 28 in Table 9.

The accounting of the carbon fed in the propane is similarly subject to a range of values. Unsaturates might contain two or three carbon atoms per mole of measured material. The liquid products could contain from one to three moles of carbon per mole of product. The term, propane and others, was determined by difference and, while extremely likely that it consists almost entirely of propane with three carbon atoms per mole, could conceivably be methane with a one to one ratio or, in the extreme, hydrogen with no carbon at all. Since the term propane and others is by far the largest, the calculations based on it will be closely reflected in the totals. The minimum, zero, in this case is rather meaningless since it is impossible for this quantity to be composed entirely of hydrogen. This minimum value is not reported in Table 9 because of this.

The accountability of the oxygen and the carbon for the runs up to number fifty was, in general, very poor. The equipment was partly dismantled after run 49 and it was found

that gases were leaking from the quench section. When these leaks were repaired, the material balances improved considerably as can be seen in Table 9. Here it will be noted that high or low values for both the carbon and the total oxygen balance occur simultaneously. This could be due to errors in either the inlet or exit gas flow rates. A high value could also be due to the presence of hydrogen in the exit gas, for both calculations were based on the premise that hydrogen was not present. If free hydrogen were present it would mean that less oxygen would be used in the water of reaction term and that some of the propane and others term would be due to hydrogen and not to propane, as assumed in the "maximum" calculations. The presence of methane or ethane in the exit gas would also have the same effect, though not as pronounced.

The low accountability of the oxygen for runs up to fifty was due to gas escaping from the quench section. This was product gas and the assumption could be made that this gas had the same composition as the gas which contained the measured quantities of products. By adjusting the measured conversions by the factor of the maximum percentage of oxygen fed found in the measured products and calculated for the water of reaction (item 27 in Table 9) new values for conversion of oxygen were found which automatically made the oxygen balance perfect. The adjusted and observed values

of percentage of oxygen fed found in total useful products is shown in Table 10 for the runs 37 to 43 with catalyst A. If the assumption made were correct, the conversions would be increased markedly in some cases.

Table 10

Adjusted Values of Conversion of Oxygen Fed to Total Useful Products

Run number	37	38	39	40	41	42	43
Observed	2.80	1.40	3.47	3.09	3.66	0.20	0.71
Adjusted	2.86	2.87	3.87	4.75	4.83	0.31	1.27

One of the recent design developments in the fluid catalytic cracking of petroleum has been the orthoflow unit of the M. W. Kellogg Company. The application of this unit to an oxidation of hydrocarbons process employing some of the principles of this investigation is shown in Figure 14. The pulsating plate fluidization would be impractical in large sizes so a conventional fluidized bed is shown here. Propane and tonnage oxygen are used to make oxygenated products.

Propane feed passes through the cooler, picking up catalyst on its way, and into the fluidized bed of the reactor. Oxygen is brought in by a separate line so that

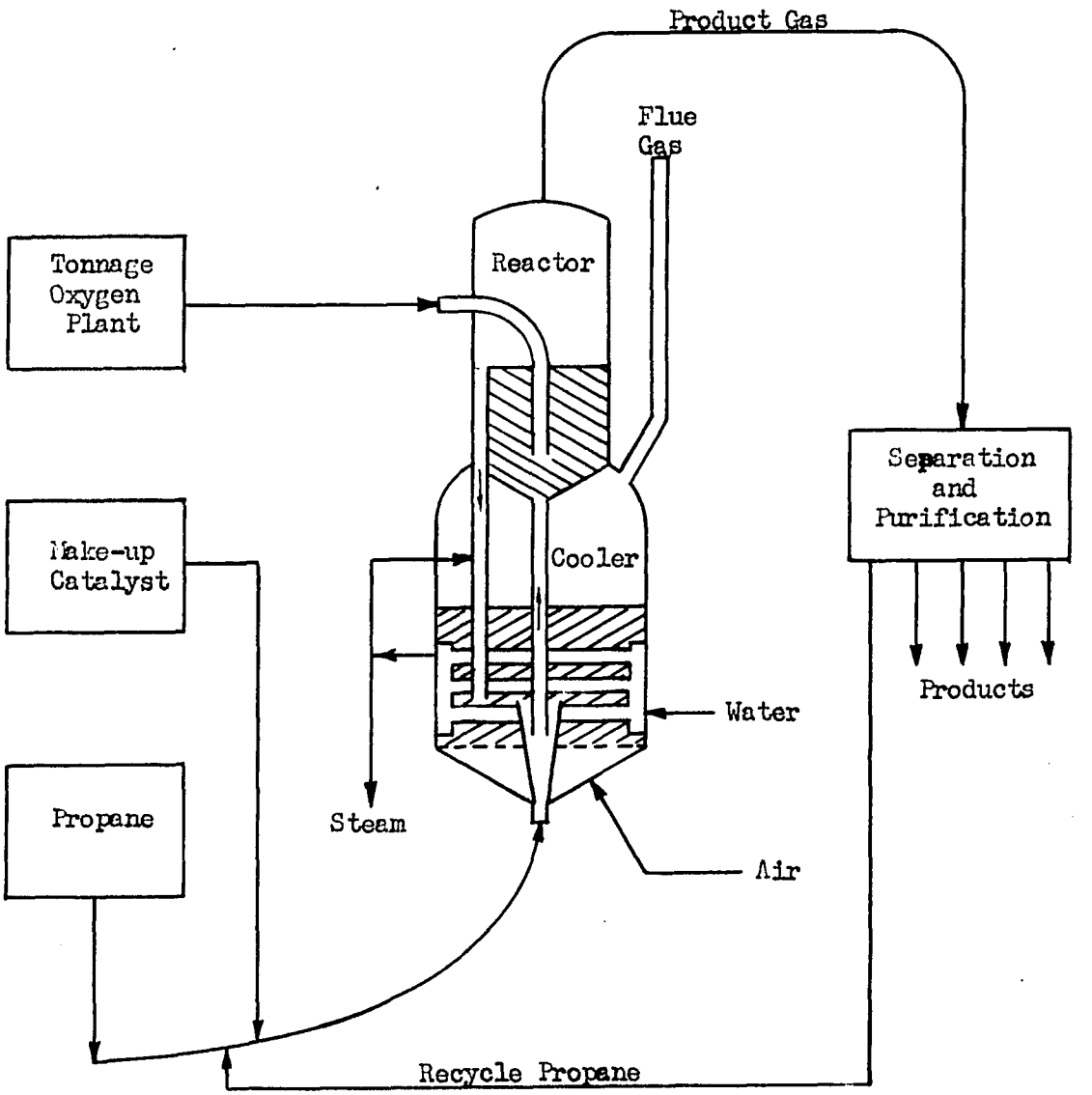

Figure 14. Application of Orthoflow Catalytic Unit to Oxidation of Hydrocarbons

the mixing takes place in the presence of the catalyst. The location of the reactor and cooler with respect to each other, as shown, reduces the length and number of bends in the catalyst lines and thereby the erosion.

Temperature control and removal of the heat of reaction are accomplished by the rapid transfer of the hot catalyst to the cooling section. The heat is removed from the cooling vessel by a heat exchanger which would act as a waste heat boiler and by the air stream which is used to maintain the cooler bed in the fluid state. The air passing through the catalyst could remove large quantities of heat which, if desired, could be recovered in a flue gas heat exchanger. If carbon were formed on the catalyst in the reactor, the air would also regenerate the catalyst. Some of the steam would be used to strip absorbed products from the catalyst flowing to the cooler.

Since the heat is liberated more rapidly in the reactor than it could be dissipated in a cooler of the same size the lower chamber would have to be somewhat larger than the reactor. Ideally, if the heat dissipation were as rapid in the cooler as its liberation were in the reactor, these two functions could be accomplished in a single vessel. Heat removal could be only by the heat exchanger in such an arrangement since the air would be unnecessary. If regeneration of the catalyst were required, another separate

vessel would be heeded.

The products and unreacted feed would be sent to a separation and purification plant from the reactor. Excess propane would be recycled.

The separation and purification plant is a major item of capital expense in present installations for oxidation of hydrocarbons, because of the complicated and hard-to-separate mixtures of products which are obtained. This points up the need for a selective catalyst. If catalysts were available to limit the products to one or two, this involved and expensive separation plant would be unnecessary. A catalyst with a high specificity would be much more desirable in this respect than one which gave a high overall yield of a mixture of products.

VI. CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations derived from this investigation are the following:

1. The advantage of temperature control possessed by a fluidized bed is well suited for application to catalytic hydrocarbon oxidation.

2. The pulsating plate apparatus developed provided a catalyst bed in a small tube similar to a true fluidized bed. The application of this type of bed is limited to small pieces of equipment because of mechanical difficulties. Its large length-to-diameter ratio limits its use also. Hot spots developed in the apparatus used, despite the presence of the catalyst.

3. The catalytic oxidation of propane depends primarily on temperature with catalysts employed, with flow rate and oxygen content of the feed being of minor importance. No product was noted below temperatures of 800° F.

4. Mixing in the presence of the catalyst was necessary to avoid run-away reactions and hot spots. High reaction temperatures and high oxygen concentrations also produced hot spots. Heat transfer capabilities of the bed could probably be improved by:

a. use of a true fluidized bed in a larger reactor,

b. use of a quench stream such as water directly above the reaction zone,

c. introduction of inerts such as nitrogen or steam in the feed, or the use of air as a feed,

d. use of relatively cool feed gases to absorb the heat of reaction,

e. circulation of catalyst to an external cooler.

5. Aldehydes and ketones were the main useful reaction products found, accompanied by smaller amounts of alcohols and, occasionally, acids. The yields of these general classes of compounds were not high enough to warrant analysis for individual compounds.

6. The best yield obtained was 3.66% of the oxygen fed converted to useful products at a bed temperature of 984° F. with an oxygen concentration of 20.6% in the feed.

7. The catalysts used were not selective, producing mixtures containing mainly aldehydes and ketones in all cases. Celite of a fluidizable grade was the basic catalyst. This material with a coating of copper oxide was used as a second catalyst and mixtures of the two were employed as two additional catalysts. The copper oxide added to the oxidation power of the Celite. Properties desirable in any

future catalyst would be promotion of the reaction at lower temperatures and a high degree of selectivity.

8. Dehydrogenation, with the formation of large amounts of unsaturated hydrocarbons always accompanied high yields of useful products, along with smaller amounts of carbon monoxide and carbon dioxide. An apparent relationship between the moles of unsaturates and the moles of useful products formed was noted. More information concerning this relationship would be desirable in any future investigation as this might be the key to the method by which the reaction proceeds. The influence of oxygen in the feed on the production of unsaturates would be interesting to know also, since it might reveal whether the useful products are formed from the unsaturates or directly from the propane.

9. Higher yields would have been realized under the conditions studied if all of the oxygen fed had reacted. The exit gases always contained unreacted oxygen. By making assumptions concerning the water formed in the reaction, an almost complete accounting of the oxygen feed could be made.

10. The investigation was limited by the apparatus to temperatures of less than 1,000° F., flow rates of 7,000 $cm.^3/min.$ and oxygen concentrations of 30%. Greater temperatures than this would be very desirable if they could be controlled properly since temperature conversion plots indicated that yields would increase further with higher

temperatures. No definite accounting could be made of all the materials fed because of physical losses and indefinite analyses. A measure of the water actually formed and a hydrogen analysis of the exit gas would help considerably in further studies.

11. The interpretation of experimental data was made extremely difficult by the complicated analyses involved and the complexity of the mixtures obtained. The analyses were time consuming and did not reveal all of the desirable information. More accurate analyses would be highly desirable.

12. The maximum conversion of fresh carbon feed, assuming propane recycle, no carbon deposition on the catalyst and maximum carbon content of the various products, was 7.4% to useful products, 85.0% to unsaturated hydrocarbons, and 7.6% to carbon monoxide and dioxide.

VII. BIBLIOGRAPHY

1. Barnett, B., Bell, E. R., Dickey, F. H., Rust, F. F. and Vaughan, W. E. Oxidations of aromatic compounds. Ind. Eng. Chem. 41:2612. 1949.

2. de Bataafsche Petroleum Maatschappij, N. V. Oxidation of saturated aliphatic hydrocarbons and their partially halogenated derivatives. Dutch patent 63,335. June 15, 1949. (Original not seen, abstracted in Chem. Abstr. 43:7502a. 1949.)

3. Bell, E. R., Dickey, F. H., Raley, J. H., Rust, F. F. and Vaughan, W. E. Oxidation of branched-chain compounds. Ind. Eng. Chem. 41:2597. 1949.

4. Bell, E. R., Irish, G. E., Raley, J. H., Rust, F. F. and Vaughan, W. E. Oxidation of ethane and related compounds. Ind. Eng. Chem. 41:2609. 1949.

5. Bludworth, J. E. Chemicals from petroleum. Petroleum Engr. 19, no. 10:146. Oct., 1948.

6. _____ Chemicals from petroleum. Oil Gas J. 45, no. 49:76. April 12, 1947.

7. _____ Engineering completed for new $15,000,000 petrochemical plant. Oil Gas J. 46, no. 35:48. Jan. 1, 1948.

8. _____ Methanol, acetone and acetaldehyde by oxidation of saturated hydrocarbon gases such as propane. U. S. patent 1,923,610 (to Hanlon-Buchanan Inc.) Aug. 22, 1933.

9. _____ Oxygenated compounds such as acetaldehyde from hydrocarbons. U. S. patents 2,128,908 and 2,128,909 (to Celanese Corp. of America) Sept. 6, 1938.

10. _____ Pentaerythritol. U. S. patent 2,333,696 (to Celanese Corp. of America) Nov. 9, 1943.

11. Bludworth, J. E. Process for the production of oxygenated organic compounds. U. S. patent 2,369,710 (to Celanese Corp. of America) Feb. 20, 1945.

12. Bone, W. A. and Drugman, J. The explosive composition of hydrocarbons. I. J. Chem. Soc. 89:660. 1906.

13. Bretton, R. H., Wan, S. W. and Dodge, B. F. Catalytic oxidation of some four-carbon hydrocarbons. Ind. Eng. Chem. 44:594. 1952.

14. Brochet, A. and Cambier, R. Ueber die Einwirkung von Formaldehyde auf die salzauren Salze des Hydroxylamins und des Monomethylamins. Comptes Rendus. 120:449. 1895. Z. Anal. Chem. 34:623. 1895.

15. The chementator. Acrolein by direct oxidation. Chem. Eng. 56, no. 11:67. Nov., 1949.

16. The chementator. Methionine: more meat on chickens. Chem. Eng. 56, no. 8:74. Aug., 1949.

17. Chemical market prices. Chem. Eng. News. 31:1045, 1143, 1247, 1487. 1953.

18. Corner, E. S. and Lynch, C. S. Oxidation carrier for hydrocarbon oxidation. U. S. patent 2,553,551 (to Standard Oil Development Co.) May 22, 1951.

19. Coward, H. F. and Jones, G. W. Limits of inflammability of gases and vapors. U. S. Bur. of Mines Bul. 279. U. S. Govt. Print. Off. 1931.

20. DeWitt, C. C. and Hein, L. B. Partial oxidation of light hydrocarbon gases at atmospheric pressure. Michigan State College. Eng. Exp. Sta. Bul. 106. 1947.

21. Egloff, G. and Alexander, M. Hydrocarbons. In Kirk, R. E. and Othmer, D. F. Encyclopedia of chemical technology. Vol. 7. p. 598-652. Interscience. New York. 1951.

22. Fischer, W. M. and Schmidt, A. A new quantitative determination of alcohols. I. The determination of methanol. Ber. 57B:693. 1924. II. The determination of ethyl alcohol and its homologs, and their separation from other substances. Ber. 59B:679. 1926. (Originals not seen, abstracted in Chem. Abstr. 18:2666. 1924. and 20:2802. 1926)

23. Fujimoto, H. Oxidation of methane. Bul. Chem. Soc. Japan. 13:281. 1938.

24. James, J. H. Partial oxidation of gaseous hydrocarbons. U. S. patent 1,558,836. June 15, 1926.

25. Kiddoo, G. Petrochemical processing. Aldehydes and alcohols by hydrocarbon oxidation. Chem. Eng. 59, no. 9:165. Nov., 1948.

26. Kooijman, P. L. Hydrogen peroxide distillation after removal of organic peroxides. U. S. patent 2,461,988 (to Shell Development Co.) Feb. 15, 1949.

27. Lacamble, A. E. H_2O_2. U. S. patent 2,376,257 (to Shell Development Co.) May 15, 1945.

28. Lind, S. C. and Bardwell, D. C. Chemical action of gaseous ions produced by α-particles. IX. Saturated hydrocarbons. J. Am. Chem. Soc. 48:2335. 1926.

29. Marek, L. F. Unit processes review. Oxidation. Ind. Eng. Chem. 40:1635. 1948.

30. _____ Unit processes review. Oxidation. Ind. Eng. Chem. 41:1892. 1949.

31. _____ Unit processes review. Oxidation. Ind. Eng. Chem. 42:1892. 1950.

32. _____ Unit processes review. Oxidation. Ind. Eng. Chem. 43:1990. 1951.

33. _____ Unit processes review. Oxidation. Ind. Eng. Chem. 44:2044. 1952.

34. Meyer, R. E. Petroleum products vs. petroleum chemicals. Chem. Eng. News. 28:1908. 1950.

35. Morgal, P. W. The catalytic vapor phase treatment of the partial oxidation products of butane. Unpublished M. S. thesis. Ames, Iowa, Iowa State College Library. 1935.

36. Mungen, R. and Kratzer, M. B. Partial combustion of methane with oxygen. Ind. Eng. Chem. 43:2782. 1951.

37. Nawrocki, P. J., Raley, J. H., Rust, F. F. and Vaughan, W. E. Oxidation of straight-chain compounds. Ind. Eng. Chem. 41:2604. 1949.

38. Newitt, D. M. and Schmidt, W. G. The oxidation of propane. II. The products of the slow oxidation at high pressures. J. Chem. Soc. p. 1665. 1937.

39. O'Connor, J. A. Dow's unique west coast plant turning out synthetic methionine by four-step process. Chem. Eng. 57, no. 4:183. April, 1950.

40. Pharmacopoeia of the United States of America. 12th revision (U. S. P.XII) Mack Printing Co. Easton, Pa. 1942.

41. Raley, J. H. and Rust, F. F. Sensitization of hydrogen bromide catalyzed reactions. U. S. patent 2,391,740 (to Shell Development Co.) Dec. 25, 1945.

42. Rust, F. F. and Bell, E. R. Catalyst separation in hydrogen bromide-catalyzed reactions. U. S. patent 2,380,675 (to Shell Development Co.) July 31, 1945.

43. Rust, F. F. and Vaughan, W. E. Controlled oxidation of paraffinic hydrocarbons. U. S. patent 2,452,326 (to Shell Development Co.) Oct. 26, 1948.

44. U. S. Bureau of the Census. Census of Manufactures: Statistics by Industry. Vol. II. 1947. U. S. Govt. Print. Off. 1949.

45. U. S. Bureau of Mines. Minerals yearbook. 1939. U. S. Govt. Print. Off. 1939.

46. _____ Minerals yearbook. 1945. U. S. Govt. Print. Off. 1947.

47. _____ Minerals yearbook. 1948. U. S. Govt. Print. Off. 1950.

48. U. S. Bureau of Mines. Minerals yearbook. 1949. U. S. Govt. Print. Off. 1951.

49. U. S. President's Materials Policy Commission. Resources for freedom. Volume IV. The promise of technology. U. S. Govt. Print. Off. 1952.

50. U. S. Tariff Commission. Synthetic organic chemicals. U. S. production and sales. 1944-1951. Reports no. 155, 157, 159, 162, 164, 169, 173, 175. U. S. Govt. Print. Off. 1946-1952.

51. Walker, J. C. and Malakoff, H. L. Basic oxygenated chemicals from C_1, C_2, and C_3 paraffins and olefins. Oil Gas J. 45, no. 33:59. Dec. 21, 1946.

52. Welty, A. B., Jr. Apparatus for the conversion of hydrocarbons. U. S. patent 2,550,741 (to Standard Oil Development Co.) May 1, 1951.

53. _____ Conversion of hydrocarbon gases to hydrogen and carbon monoxide. U. S. patent 2,550,742. (to Standard Oil Development Co.) May 1, 1951.

54. Wiezevich, P. J. and Frolich, P. K. Direct oxidation of saturated hydrocarbons at high pressures. Ind. Eng. Chem. 26:267. 1934.

55. Williams, R., Jr. Why the formaldehyde boom? Chem. Eng. 58, no. 9:369. Sept., 1951.

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IX. APPENDICES

APPENDIX A. ANALYSES

The gas coming from the reactor contained the reaction products and the unreacted portions of the feed. The condenser, cold trap and absorbers collected all of the liquid products including alcohols, aldehydes, ketones, acids and water. The gas which was measured in the wet test meter contained gaseous oxygenated products such as carbon dioxide and carbon monoxide, unreacted oxygen, and propane, as well as other possible hydrocarbon products which would result from the fracture of the propane molecule. These other hydrocarbons might include methane and ethane as well as unsaturates, ethylene, propylene or acetylene, for example. Hydrogen might also be present.

The actual volume of the gas during a timed run was obtained from the wet test meter data. A 250 ml. gas sampling tube of this gas was taken during the run and was later subjected to a standard Orsat apparatus analysis. The gas analysis determined the volume percentages of carbon dioxide, carbon monoxide, oxygen and unsaturated hydrocarbons by chemical absorption. The absorbing solutions used in the Orsat type gas analysis were the following:

1. For carbon dioxide: a 30% solution of potassium hydroxide.

2. For unsaturated hydrocarbons: an excess of liquid bromine in a solution containing 5% of potassium hydroxide.

3. For oxygen: an equal volume of a 15% solution of pyrogallic acid in water and 30% potassium hydroxide.

4. For carbon monoxide: a solution of 11.5 grams of cuprous chloride in 43 ml. of concentrated ammonium hydroxide and 50 ml. of water.

The remainder of the gas was listed as propane and others. The major portion was unreacted propane, but saturated hydrocarbons, such as methane and ethane, and hydrogen would also be contained in this amount. This analysis and the dry volume of the gas obtained from the wet test meter gave a measure of the total amount of these components present.

Liquid products were obtained in the condenser, the cold trap and the absorbers. Early tests showed that not all of the product formed during a 30 minute run could be absorbed in the first five water absorbers. Aldehydes and ketones were present in the gas after it passed through the water. To retain these products, three absorbers containing 2,4-dinitrophenylhydrazine were inserted in the absorber train. This material forms a precipitate with all aldehydes and ketones. The last two water absorbers were used as a check to see that no products survived the preceding absorbers.

The absorbing liquid from the first five absorbers was combined with the liquid obtained from the condenser and the cold trap and the rinse water from all three and made up to 2,000 ml. in a volumetric flask. Portions of this volume were then taken for analysis. An acid analysis was made using sodium hydroxide (40). The aldehydes and ketones in the liquid solution were determined using the hydroxylamine hydrochloride method of Brochet and Cambier (14). In this method the acid released when a neutral solution of aldehydes or ketones is treated with hydroxylamine hydrochloride is titrated with a standard potassium hydroxide solution. Alcohol was determined according to the method of Fischer and Schmidt (22). In this determination the alcohol is reacted with nitrous acid to form the volatile nitrite ester which is swept out in a current of carbon dioxide and subsequently absorbed in a potassium iodide solution containing hydrochloric acid. The iodine released is then titrated with standard thiosulfate solution.

These tests gave the number of moles of the indicated products which could be converted immediately to moles of oxygen. However, after the 2,4-dinitrophenylhydrazine precipitate obtained was weighed, it gave a weight containing a number of moles depending on the type of the compound. Because of the high molecular weight of the absorbing agent (M.W. = 198), the absorption products formed for different

compounds vary comparatively little. The molecular weights of the formaldehyde, acetaldehyde and acetone derivatives are 208, 222 and 236 respectively. Thus an error of about 10% at most would be introduced by assuming that the precipitate was all of one compound. The precipitate was found to contain less than 10% of the total aldehydes and ketones, which makes the error involved considerably less when carried into the total weight figure. The precipitate was calculated as the formaldehyde derivative.

After all solutions and equipment had been prepared, the gas analysis required one hour and the liquid analysis, three hours.

APPENDIX B. SAMPLE CALCULATION

A sample calculation for run 51 follows. The data taken during the run were:

Barometer data	
Pressure	28.766 in. Hg.
Temperature	76° F.
Correction	-0.001 in. Hg.
Time of product collection	30 min.
Temperatures	
Oxygen at rotameter	83.9° F.
Propane at rotameter	84.1° F.
Room	83.9° F.
Cold trap liquid	-37.5° C.
Gas out of quench	140° F.
Oxygen into reactor	881° F.
Propane into reactor	954° F.
Mixed gases at reactor bottom	942° F.
1 in. above reactor bottom	945° F.
13 in. above reactor bottom	930° F.
Reactor exit	273° F.
Pressures	
Oxygen rotameter	44.8 cm. Hg. gauge
Propane rotameter	46.25 cm. Hg. gauge
Reactor bottom	44.0 cm. Hg. gauge
Across reactor	5.85 cm. water
Condenser entrance	41.2 cm. Hg. gauge
Reactor top	43.8 cm. Hg. gauge
Entrance to exhaust line	0.9 cm. Hg. vacuum gauge
Propane cylinder	76 psig.
Propane delivery	12 psig.
Oxygen cylinder	1270 psig.
Oxygen delivery	12 psig.
Nitrogen cylinder	200 psig.
Nitrogen delivery	11 psig.
Rotameter readings	
Oxygen	73
Propane	125
Catalyst charged	105.4 gm.
Catalyst recovered	95.4 gm.
Carbon on catalyst	negligible

The voltage and current of each heater were measured.
Samples taken
Exit gas
Condenser product volume 14.5 ml.
The liquid from the condenser, cold trap and absorbers 1, 2, 3, 4 and 5 was collected and made up to 2,000 ml.
The 2,4-dinitrophenylhydrazine precipitate from absorbers 6, 7 and 8 was collected and combined.
The liquid from absorbers 9 and 10 produced a negative test for aldehydes and ketones.

Results of analyses

Exit gas, volume %, dry basis

Carbon dioxide	3.0
Unsaturated hydrocarbons	9.4
Oxygen	0.9
Carbon monoxide	1.4
Propane and others, by difference	85.3
Total	100.0

Liquid

Acids	0.371 mg. moles
Aldehydes and ketones in liquid solution	43.06 mg. moles
in 2,4-dinitrophenylhydrazine (as formaldehyde)	4.12 mg. moles
total	47.18 mg. moles
Alcohols	6.602 mg. moles

The calculations based on these data are as follows:

Pressure

Barometric pressure corrected for temperature

$$(28.766 - 0.001) - 0.0026(76.0 - 28.5) = 28.641 \text{ in. Hg.}$$

Room pressure (barometer on higher floor)

$$28.641 + 0.012 = 28.653 \text{ in. Hg.}$$

Reactor pressure

$$28.653 + 44.0/2.54 = 45.976 \text{ in. Hg.}$$

Feed

Oxygen: from a calibration curve it was found that a reading of 73 at 80° F. and 29.00 in. Hg. would correspond to an actual flow rate of oxygen of 512 cm^3/min. measured at 14.7 psia. and 70° F. The actual flow rate is

$$(512)\left(\frac{28.653 + 44.8/2.54}{29.00}\right)^{\frac{1}{2}}\left(\frac{460 + 80}{460 + 83.9}\right)^{\frac{1}{2}}$$

$= 644$ cm^3/min. at 14.7 psia. and 70° F.

Propane: from a calibration curve it was found that a reading of 125 at 80° F. and 29.00 in. Hg. would correspond to an actual flow rate of propane of 4770 cm^3/min., measured at 14.7 psia. and 70° F. The actual flow rate is

$$(4470)\left(\frac{28.653 + 46.25/2.54}{29.00}\right)^{\frac{1}{2}}\left(\frac{460 + 80}{460 + 84.1}\right)^{\frac{1}{2}}$$

$= 6041$ cm^3/min. at 14.7 psia. and 70° F.

The values in Table 11 are then calculated.

Table 11

Feed Calculation. Run 51

	Oxygen	Propane	Total
Flow rate, cm^3/min.[a]	644	6,041	6,685
Feed composition, volume %	9.63	90.37	100.00
Total volume fed, cm^3[a]	19,320	181,230	200,550
Mg. moles fed[b]	800	7,506	8,306
Mg. moles carbon fed	0	22,518	22,518
Weight fed, gm.	25.6	330.9	356.5

[a]At 14.7 psia. and 70° F.

[b]Molar volume at 14.7 psia. and 70° F. is 24,145 cm^3.

Superficial velocity:

Free cross section of reactor: 1.376 sq. in.

$$\frac{6{,}685\ cm^3}{min.} \times \frac{1}{1.376\ in.^2} \times \frac{ft.}{12\ in.} \frac{min.}{60\ sec.}$$

= 0.412 ft./sec. at 14.7 psia. and 70° F.

Value of F/W:

Weight of catalyst: 100.0 gm.

$$\frac{F}{W} = \frac{356.5\ gm.}{30\ min.} \times \frac{60\ min.}{hr.} \times \frac{1}{100.0\ gm.} = 7.13/hr.$$

Exit gas:

Vapor pressure of water at 28.0° C. is 28.439 mm. Hg.

The volume of dry exit gas at 14.7 psia. and 70° F. would be

$$(202{,}200)\left(\frac{28.653 - 0.35 - 28.349/25.4}{29.92}\right)\left(\frac{460 + 70}{460 + 82.4}\right)$$

= 179,530 cm^3 at 70° F. and 14.7 psia.

= 7,435 mg. moles.

Material Distribution

Oxygen

The yields of the various products and the oxygen contained in them, in mg. moles, are then calculated on the basis of the dry exit gas and liquid product analyses. This amount of oxygen found directly in the measured products is

then expressed as a percentage of the oxygen fed (800 mg. moles). These results are found in the first three columns of figures in Table 12.

Some of the oxygen would also be combined with the hydrogen which originally was in the converted propane but does not appear in the products. The maximum amount of oxygen which could be used in this way is in combination with the hydrogen as water. If this is assumed to happen, the amount of hydrogen liberated and the water formed can be calculated on the basis of the products measured. For some of these products such as carbon monoxide or carbon dioxide, the amount of oxygen found in this water of reaction is a definite amount, but since the other measurements are not of single compounds but of classes, with the amount of oxygen found in the water of reaction dependent on the actual compounds, only the upper and lower limits of the oxygen content can be given. Using propane and water as the only sources of hydrogen and the indicated product and water as the only hydrogen containing products, the oxygen found in the water of reaction for various products and the assumed reaction is given in Table 13. The unsaturated hydrocarbons have been assumed to contain only double and no triple bonds.

The maximum and minimum amounts of oxygen which could be found in the water of reaction, assuming all hydrogen not

Tat

Material Distr

Product			Distribution of oxygen fed, %	In product
Gaseous products				
Carbon dioxide	7435x0.030 =	233.0	27.9	233.0
Unsaturated hydrocarbons	7435x0.094 =	699.0	—	—
Oxygen	7435x0.009 =	66.9	8.4	66.9
Carbon monoxide	7435x0.014 =	104.1	6.5	52.2
Propane and others	7435x0.853 =	6342.0	—	—
Total gaseous		7435.0	42.8	341.1
Liquid products				
Acid		0.371	0.046	0.37
Alcohol		6.602	0.413	3.30
Aldehydes and ketones		47.18	2.95	23.59
Total liquid		54.153	3.409	27.26
Grand total		7489.0	46.2	369.4
Percent accounted for				46.2

Table 12

Material Distribution. Run 51

tribution oxygen sd, %	Oxygen, mg. moles					Carbon, mg. moles	
	In product	In H_2O of reaction		Total			
		Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
27.9	233.0	148.8	148.8	371.8	371.8	223.0	223.0
—	—	350.0	233.0	350.0	233.0	2097.0	1398.0
8.4	66.9	—	—	66.9	66.9	—	—
6.5	52.2	69.4	69.4	121.6	121.6	104.1	104.1
—	—	—	—	—	—	19026.0	0.0
42.8	341.1	568.2	451.2	910.3	793.3	21450.0	1725.1
0.046	0.37	0.186	0.062	0.56	0.43	1.113	0.371
0.413	3.30	0.0	-2.201	3.30	1.10	19.806	6.602
2.95	23.59	23.59	7.863	47.18	31.45	141.54	47.18
3.409	27.26	23.776	5.724	51.04	32.98	162.46	54.15
46.2	369.4	592.0	456.9	961.3	826.3	21612.0	1779.2
	46.2	74.0	57.1	120.2	103.3	96.0	7.9

Table 13

Oxygen in Water of Reaction for Various Products

Product	Assumed reaction	Moles O_2 in water / Mole of product
Carbon monoxide	$C_3H_8 + 3.5\ O_2 \rightarrow 3\ CO + 4\ H_2O$	2/3
Carbon dioxide	$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$	2/3
Unsaturated hydrocarbons		
Maximum	$C_3H_8 + 0.5\ O_2 \rightarrow C_3H_6 + H_2O$	1/2
Minimum	$2\ C_3H_8 + O_2 \rightarrow 3\ C_2H_4 + 2\ H_2O$	1/3
Acids		
Maximum	$C_3H_8 + 1.5\ O_2 \rightarrow C_2H_5COOH + H_2O$	1/2
Minimum	$C_3H_8 + 3.5\ O_2 \rightarrow 3\ HCOOH + H_2O$	1/6
Alcohols		
Maximum	$C_3H_8 + 0.5\ O_2 \rightarrow C_2H_7OH$	0
Minimum	$C_3H_8 + 2\ H_2O + 0.5\ O_2 \rightarrow 3\ CH_3OH$	-1/3
Aldehydes and ketones		
Maximum	$C_3H_8 + O_2 \rightarrow CH_3COCH_3 + H_2O$	1/2
Minimum	$C_3H_8 + 2\ O_2 \rightarrow 3\ HCHO + H_2O$	1/6

found in the actual products has been converted to water, are calculated and indicated in Table 13. The total accountable oxygen found in the product and in the water of reaction is found on the basis of these assumptions.

An estimate of the amount of water actually formed could be made from the water in the condenser product and the water in the exit gas passing through the condenser product receiver. Distillation was ineffective in separating any useful products from the water in the condenser product so that the assumption that it is 95% water is conservative. The receiver will be assumed to be at the wet test meter temperature. The mg. moles of water formed is:

In the condenser liquid product:

$$\frac{14.5 \times 0.95}{0.01802} = 764 \text{ mg. moles}$$

In the exit gas saturated with water at 28° C.:

$$\frac{7.435 \times 1.116}{27.187} = 306 \text{ mg. moles}$$

Total = 764 + 306 = 1070 mg. moles

This represents 535 mg. moles of oxygen, an amount which is between the minimum and maximum values calculated on the basis of previous assumptions, indicating the validity of these assumptions and the probability that there was little free hydrogen in the exit gas.

Since there is a minimum and maximum value for the water of reaction there will also be a minimum and maximum

"total" value. Totals for the gaseous products, the liquid products, and grand totals are also indicated.

Carbon

The mg. moles of carbon fed is taken from Table 11. The number of moles of carbon in the various products is shown in Table 14, with the minimum and maximum values shown for each type of product found. The calculated maximum and minimum values are shown in the last two columns of Table 12. These calculations can account for a maximum of 96.0% of the carbon fed.

Table 14

Moles of Carbon in Various Products

Product	Moles of carbon per mole of product			
	Maximum		Minimum	
	Compound	Value	Compound	Value
Carbon monoxide	CO	1	CO	1
Carbon dioxide	CO_2	1	CO	1
Unsaturated hydrocarbons	C_3H_6	3	C_2H_4	2
Propane and others	C_3H_8	3	H_2	0
Acids	C_2H_5COOH	3	HCOOH	1
Alcohols	C_3H_7OH	3	CH_3OH	1
Aldehydes and ketones	CH_3COCH_3	3	HCHO	1

The air used for the cooling of the apparatus would probably have burned off any carbon which had deposited on the catalyst. An ignition of the recovered catalyst revealed that there was no carbon retained on it.

The conversion of the 22,518 mg. moles of carbon feed, based on the maximum carbon content as shown in Table 12, is:

Carbon dioxide	1.0%
Unsaturated hydrocarbons	9.3
Carbon monoxide	0.5
Acids	0.01
Alcohols	0.09
Aldehydes and ketones	0.63
Total	11.52%

If it is assumed that the remainder of the carbon, 88.5%, survives as propane in the exit gas, and that the propane were recycled, the conversion of fresh carbon feed would be:

Unsaturated hydrocarbons		81.1%
Carbon dioxide		8.6
Carbon monoxide		4.0
Useful products		
Acids	0.04	
Alcohols	0.77	
Aldehydes and ketones	5.47	
Total useful products		6.3
Total		100.0%

Thus, if unreacted propane were recycled, the useful products would represent a maximum of 6.3% of the carbon fed and unsaturated hydrocarbons would account for 81.1% of the carbon fed. Carbon monoxide and dioxide would account for the remaining 12.6% of the new carbon feed.

APPENDIX C. PREPARATION OF CATALYSTS

The original catalyst used was Celite, a product of the Johns Manville Company. It is a diatomaceous earth -- a mixture of silica and alumina and its size distribution is such that it will all pass through a 50 mesh screen and all be retained on a 140 mesh screen. The company specifications on it are C. C. C. Type IX, C-32397, a type of commercial cracking catalyst. It was designated catalyst A.

Catalyst B was made by depositing a coating of copper oxide on catalyst A in the following manner. Two hundred grams of catalyst A were subjected to a vacuum of 63.5 grams of mercury for exactly ten minutes. At the end of this time a solution of 61.5 grams of $Cu(NO_3)_2 \cdot 3H_2O$ in 130 ml. of water was added. This amount of solution just barely wetted all of the catalyst after being shaken in the evacuated flask quite vigorously, and gave the catalyst a uniform blue color. The catalyst with the solution on it was then subjected to a pressure of 20.8 cm. of mercury for an additional ten minutes.

The material was then taken from the flask and spread out to air dry overnight. After the air drying this copper nitrate coated catalyst was ignited to convert the copper nitrate to copper oxide. The ignition was performed under a continuous tumbling action in the apparatus shown in

Figure 15. The ignition chamber was made of a 11.5 inch length of three inch pipe with a removable cap on the end. A shaft of 3/4 inch pipe was connected to this with a tee in it to act as a vent for the liberated fumes. A pulley on the shaft made it possible to rotate the apparatus at a speed of 6.75 rpm. with the motor and gear reducer shown. A thermocouple was placed in a glass tube which extended into the ignition chamber to indicate the temperatures reached.

The chamber was heated from the outside by four Fisher burners and it was possible to attain a temperature of over 1200° F. within the chamber. During the heating, the copper nitrate was converted to cupric oxide, CuO, and nitrogen dioxide, NO_2. The nitrogen dioxide with the water of hydration, came off in thick reddish-brown fumes during the ignition, requiring operation in a hood. After the fumes had ceased the heating was continued for five minutes. The product obtained from this treatment was of a uniform gray color, with no agglomeration of particles into larger pieces. It thus had virtually the same size characteristics as the Celite which was used as the carrier. This catalyst was designated catalyst B. One large batch was made up and used for all tests and further blending.

Tests on this catalyst indicated that its oxidizing power was too strong. Catalyst C was made up of a 50 - 50 mixture of catalysts A and B. Catalyst D was made up of 75% catalyst B and 25% catalyst A.

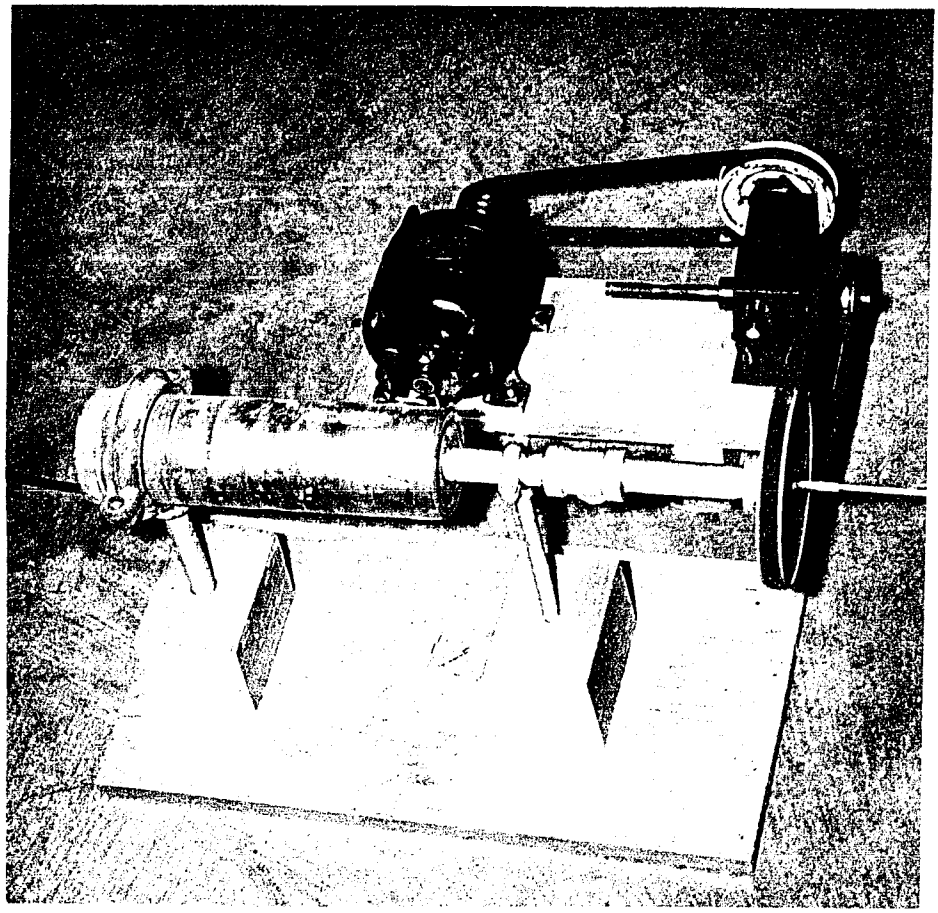

Figure 15. Catalyst Activator